Vol. XXVIII. [MAY, 1906.] No. 5.

THE JOURNAL

OF THE

American Chemical Society

EQUILIBRIUM IN THE SYSTEM BERYLLIUM OXIDE, OXALIC ANHYDRIDE AND WATER.

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Received February 12, 1906.

I. THE OXALATES OF BERYLLIUM.

THE attempts of Vauquelin, 1798,[1] and of Debray, 1855,[2] to prepare the normal oxalate of beryllium resulted only in the formation of an indeterminate gummy mass. Their failure was due to the fact, only recently fully comprehended, that definite crystalline compounds of beryllium can be made only when exact equivalents of anion and cation are present or when there is an excess of the acid component. Atterberg, 1873,[3] had the same experience but gave the formula $BeC_2O_4.Be(OH)_2.H_2O$ to the gummy mass first obtained and $BeC_2O_4.6Be(OH)_2.6H_2O$ to the highly basic precipitate obtained by diluting the solution of the first with a large excess of water. Rosenheim and Woge, in 1897,[4] first prepared the normal oxalate $BeC_2O_4.3H_2O$ and described an acid salt, $2BeC_2O_4.H_2C_2O_4.5H_2O$, which, if it exists, is the only acid salt of beryllium known, with the possible exception of some very doubtful acid selenites described by Nilson,[5] the also doubtful acid arsenate and phosphate of Atterberg[6] and Scheffer's[7] acid

[1] Allgem. J. Chem. 1, 590.
[2] Ann. chim. phys. [3] 44, 37.
[3] Kgl. Svenska Akad. Handl. 12, 51.
[4] Z. anorg. Chem. 15, 283.
[5] Bull. soc. chim. [2] 23, 355.
[6] Ofvegt. Akad. For. (Stockholm) 1875, No. 7, 33.
[7] Ann. 109, 144.

phosphates. Wyrouboff[1] confirms the results of Rosenheim and Woge as to the normal oxalate, although he claims for it the formula consistent with the completely discredited trivalency of beryllium. With the exception of Vauquelin all of the above-mentioned investigators, as well as Philipp,[2] made well-characterized double oxalates with the alkaline metals, but these double oxalates have no connection with the present paper.

The following oxalates of beryllium have therefore more or less standing in chemical literature:

$BeC_2O_4.H_2O$
$BeC_2O_4.3H_2O$
$2BeC_2O_4.H_2C_2O_4.5H_2O$
$BeC_2O_4.Be(OH)_2.H_2O$
$BeC_2O_4.6Be(OH)_2.6H_2O$

Attempts were made by us to prepare and study all of these substances and any other compound containing the three components, BeO, C_2O_3 and H_2O, that might be found under varying equilibrium conditions.

Purification of Material.—Previous work by one of us[3] had shown that the basic acetate of beryllium, discovered by Urbain and Lacombe,[4] possessed decidedly characteristic properties which might be applied to separating beryllium from aluminum and iron, the only two elements which present any real difficulty. It is easily sublimed and is soluble in glacial acetic acid, benzene, toluene, chloroform, all petroleum distillates, alcohols, ether, carbon disulphide, carbon tetrachloride, acetone, etc., to a greater or less extent. Iron and aluminum form no similar compound, and Haber and Van Oordt[5] have already proposed to separate their normal acetates from the basic acetate of beryllium by means of the solubility of the latter in chloroform. Parsons[6] has shown that glacial acetic acid is itself, when hot, a most excellent solvent for the basic acetate of beryllium, allowing the basic acetate to crystallize out on cooling in beautiful octahedra. We tried the effect of many solvents but found that none of them compared with glacial acetic acid for ease of manipulation and recrystalliza-

[1] Bull. soc. franç. min. 25, 71.
[2] Ber. 16, 752.
[3] Parsons: This Journal, 26, 721.
[4] Compt. rend. 133, 874.
[5] Z. anorg. Chem. 40, 465.
[6] This Journal, 26, 738.

tion of the product, and since the small amounts of the acetates of iron and aluminum, which are soluble in this reagent when hot, are not precipitated on cooling it, offered a ready means of purification.

Commercial beryllium hydroxide, containing notable quantities of iron and aluminum, was dissolved in acetic acid, evaporated and dried. The pulverized residue was boiled with glacial acetic acid and filtered through a funnel surrounded by a steam coil. On cooling, small octahedra of basic beryllium acetate separated in quantity. These were collected on a Buchner funnel and washed twice with cold glacial acetic acid. The residue was retreated with the same acetic acid. This can not be done continuously for the reason that the beryllium acetate first formed by solution of the hydroxide and evaporation always undergoes hydrolysis so that the residue, no matter how carefully dried, always contains beryllium hydroxide and yields more or less water to the glacial acetic acid. The presence of water, except in very small quantities, is fatal to the formation of the basic acetate, and even in small quantities causes a loss of beryllium in the mother-liquors. This can be recovered, however, by evaporation and retreatment. The crystals of beryllium basic acetate were recrystallized from glacial acetic acid and obtained pure. Some of this basic acetate was sublimed for further purification, but this was found to add but little to the quality of the product.

By far the most convenient compound of beryllium to use in the laboratory as a basis for the preparation of other compounds is the basic carbonate. Although of indefinite composition an analysis of any given preparation is easily made by simple ignition in platinum. To prepare this substance the basic acetate was hydrolyzed by hot water and dissolved by the addition of a slight excess of pure acetic acid. It was then precipitated by ammonia, filtered, dissolved in ammonium carbonate and precipitated by boiling with steam. The perfectly white and granular precipitate was washed and dried.

Analysis gave BeO = 43.03 per cent. and 43.08 per cent.

Beryllium Oxalate Trihydrate, $BeC_2O_4 + 3H_2O$.—Basic beryllium carbonate was treated with a slight excess above the equivalent amount of oxalic acid and dissolved readily with effervescence. On evaporation, needle-like crystals of oxalic acid separated out first and were removed. On further evaporation, orthorhombic

crystals of a beryllium oxalate were deposited which contained notable quantities of oxalic acid. These crystals were dissolved and recrystallized, rejecting again the needle-like crystals of oxalic acid first deposited, and this operation was repeated nine times without securing crystals free from occluded oxalic acid. The separation is rendered very difficult, if not impossible, from the comparatively great solubility of both substances and from the fact that, at ordinary temperatures at least, they differ but little in solubility.

Analyses of the last five crops of crystals showed the following composition.

	BeO.	C_2O_3.	BeO/C_2O_3.
5	15.05	49.06	1.18
6	15.43	49 41	1.12
7	15.35	48.61	1.11
8[1]	16.90	51.87	1.07
9	15.85	48.68	1.06

Both Rosenheim and Woge[2] and Wyrouboff[3] claimed to obtain two forms of crystals of the normal oxalate of beryllium, the first needle-like and the second in plates. It is noteworthy that we were able to obtain only the latter form of crystals, and that invariably the first crops of these were mixed with needle-like crystals easily separated under the microscope and which proved to be oxalic acid in every instance. We were also unable to secure the pure oxalate by the method they used.

The pure normal oxalate was obtained in beautiful orthorhombic crystals by adding to the slightly acid oxalate of the ninth recrystallization the exact amount of basic beryllium carbonate necessary to neutralize the occluded oxalic acid. The crystals gave, on analysis, the theoretical composition of $BeC_2O_4.3H_2O$.

Great care was necessary that no excess of the carbonate be used or the oxalate would not crystallize but would simply evaporate to a thick, gummy glucose-like mass. So small an excess as 0.1 per cent. of the oxide completely prevented crystallization, and this apparently small amount added for experimental purposes must in reality have been larger than necessary for attempts to recrystallize the pure oxalate itself

[1] 8 had lost some of its water of crystallization.

[2] Z. anorg. Chem. 15, 283.

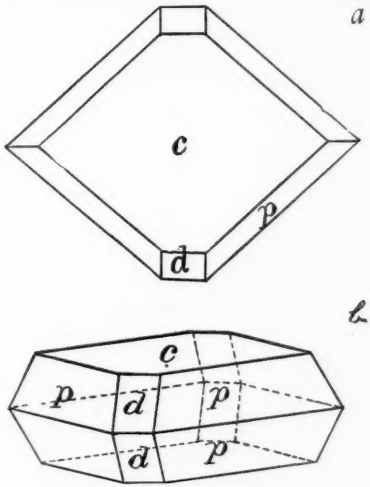
[3] Bull. soc. franç. min. 25, 71.

failed in several instances until a drop of oxalic acid solution was added, apparently from no other reason than a slight loss of oxalic acid when the crystals were dissolved in hot water and evaporated on the steam-bath. The addition of small crystals of the normal oxalate to the uncrystallizable mass in no wise affected the result.

Beryllium oxalate is stable at room temperature. It is soluble in less than its own weight of water at 100° and is but little less soluble at ordinary temperatures. It is strongly acid in reaction, like all normal salts of beryllium, has a rather sharp, sweet taste and is easily decomposed by heat. It readily dissolves a large amount of its own carbonate, forming liquid and solid basic solutions as later described.

Through the courtesy of Prof. Samuel L. Penfield and Mr. F. H. Heath, who most kindly examined the crystals for us, we are able to add the following crystallographic characteristics.

Crystals of $BeC_2O_4.3H_2O$.—The crystals are orthorhombic, and the accompanying projections show the general development. The forms are as follows: *c* (001), *d* (101) and *p* (111).



The crystals were not very well suited for measurement with the goniometer, but the best ones were selected and the following observations made:

$p \wedge p'''$, $111 \wedge 1\bar{1}1 = 74° 16'$*
$p \wedge p'$, $111 \wedge \bar{1}11 = 90° 6'$*
$c \wedge p$, $001 \wedge 111 = 68° 30'$.
Calculated, 68° 20'.

The measurements marked by an asterisk yield the axial ratio $a:b:c = 0.853:1.0:1.645$.

The *d* faces were so small and poorly developed that no satisfactory reflections could be obtained from them. On a second crop of crystals the *d* faces were absent and there was a greater development of the basal plane than shown in the accompanying figures, the crystals appearing as flat tables with beveled edges.

No distinct cleavage was observed. With a tabular crystal examined under the polariscope, it was seen that the *c* axis was a bisectrix, and that the plane of the optical axes was the brachypinacoid. The interference figure was, however, very indistinct and the axial angle was so large that the hyperbolas opened out beyond the field of view.

Beryllium Oxalate Monohydrate, $BeC_2O_4 + H_2O$.—This oxalate is easily prepared by heating the trihydrate to 100–105°, at which temperature it is stable as well as at lower temperatures, if in dry air. Heated much above these temperatures it begins to lose water slowly but more rapidly as the temperature approaches 220°, about which temperature the oxalate begins to decompose, and at 350° is completely converted into the oxide. There is no apparent stage between the formation of the anhydrous oxalate and its decomposition, but decomposition sets in before all the water is driven off as in the case with the sulphate.

Acid Beryllium Oxalate.—The acid oxalate described by Rosenheim and Woge[1] could not be prepared although their directions were carefully followed and modifications tried. A single experiment is characteristic. Beryllium carbonate was dissolved in twice its equivalent of oxalic acid and subjected to fractional crystallization over sulphuric acid. The crystals of the first three crops were long and needle-like and gave no tests for beryllium. The fourth crop contained two forms, one long and needle-like, the other in orthorhombic plates. They were carefully separated under the microscope and the former proved to be only oxalic acid. In no case could a beryllium oxalate be obtained, after mechanically separating the admixed oxalic acid, that con-

[1] Z. anorg. Chem. 15, 283.

tained a ratio of C_2O_3 to BeO greater than 1.18 to 1, due to occlusion of oxalic acid, while the crystals described by Rosenheim and Woge were assigned the formula $2BeC_2O_4.H_2C_2O_4.5H_2O$.

It had been our expectation to examine this oxalate in contact with its mother-liquors in a thermostat, as was done with the basic precipitates, to be described later, for the concentration of the mother-liquors would have shown at once whether it was a single phase or mixed crystals but the fact that the mixed crystals could be so easily separated mechanically under the microscope rendered this part of the work entirely unnecessary. We were unable to procure any single phase which even approached the acid oxalate of Rosenheim and Woge. The further consideration that no other well-authenticated acid salt of beryllium is known leads us to the conclusion that the existence of an acid oxalate of this metal is highly improbable.

Basic Beryllium Oxalates.—One of us[1] has already pointed out the property possessed by solutions of any of the salts of beryllium of dissolving large quantities of beryllium hydroxide giving rise to solutions decidedly basic in character, although acid in reaction, and which for the most part are precipitated by dilution with water after a certain concentration of the BeO component has been reached. The oxalate is perfectly analogous to the sulphate[2] in this respect, giving rise to both soluble and insoluble basic substances of indefinite composition.

Soluble Basic Oxalates.—If a hot saturated solution of oxalic acid is treated with an excess of basic beryllium carbonate or hydroxide, it dissolves the basic component until a concentration of 2.85 BeO to 1 C_2O_3 is reached, setting free carbon dioxide and giving rise to a thick syrupy solution. Any excess of carbonate, so long as the mass remains moist, also loses its carbon dioxide but remains insoluble in the form of the so-called solid basic oxalates to be described in the next section. The colorless solution still reacts acid to litmus. On drying, it becomes more and more viscous and finally glassy without the slightest evidence of crystalline structure. When diluted with water a white voluminous precipitate settles out. If solutions of oxalic acid growing less and less concentrated are used, the ratio of base soluble in the acid grows constantly smaller. No matter whether this con-

[1] Parsons: This Journal, **26**, 1437.

[2] Ibid. **26**, 1438.

centration is 2.85 BeO: 1 C_2O_3 or only a very slight (less than 0.1 per cent.) excess over the ratio BeO: C_2O_3, the residues on evaporation are glutinous and glassy in character and are physically indistinguishable except that the compounds of higher ratio are soluble only in a minimum of water while, at least, those less than 1.5 BeO to 1 C_2O_3 will dissolve in any amount used.

A single experiment shows this relation clearly. Two cc. of the solution 2.85 BeO: 1 C_2O_3 were treated with successive quantities of water of 10 cc. each from concentration 1 to 0.01, then with 100 cc. portions. Each 10 cc. added caused a precipitate and each 100 cc. did the same until a concentration of 0.001 was reached, after which further dilution appeared to be without effect and the ratio of base to acid remained approximately 1.5: 1. On evaporating any one of these concentrations a glue-like film formed, hardened and became glassy. If a solution of concentration 0.001 was boiled down to small bulk, a small amount of a fine white precipitate settled out, resembling magnesium ammonium phosphate to the naked eye but showing no crystalline structure under the microscope.

The following table shows the composition of these soluble basic oxalates. The concentration is expressed in the first column in the ratio of cubic centimeters of saturated solution to cubic centimeters of water. A gram concentration would undoubtedly be preferable but in this case serves no useful purpose.

Concentration.	Ratio BeO/C_2O_3.
1 : 5	2.1 : 1
1 : 50	1.9 : 1
1 : 100	1.74 1
1 : 1000	1.5 . 1

These results were obtained at ordinary temperatures and as the reaction takes place more and more slowly with the dilution it is probable that complete equilibrium was reached in no instance.

The oxalate 2: 1 is the one to which Atterberg[1] gives the formula $BeC_2O_4.Be(OH)_2.H_2O$ but it can have no claim to being a definite chemical compound. It is simply a degree of saturation and, except as shown by analysis, can not be distinguished from any other ratio near to its own. On drying at 100° the amount of water left is generally in excess of the theoretical amount necessary to produce the hydroxide, but this has little significance as the gummy character of the substances make their complete drying

[1] Kgl. Svenska Akad. Handl. 12, 51.

improbable. As it is impossible to obtain any degree of saturation that will yield a solid and liquid phase together for any concentration between 1.5 BeO: 1 C_2O_3 and 1 BeO: 1 C_2O_3 it is, of course, out of the question to apply the phase rule considerations used on the insoluble basic oxalates next to be considered.

Insoluble Basic Oxalates.—Rosenheim and Woge did not succeed in producing any oxalate of beryllium of greater basicity than 2.8 BeO to 1 C_2O_3, although they refer to Atterberg's work. This failure could have been due to no other cause than wrong conditions, for these highly basic precipitates are thrown out of any solution of the oxalate of a bascity greater than about 1.5 to 1 when sufficiently diluted with water, and the extent of the dilution necessary for precipitation to begin varies inversely as the basicity of the solution. The action is in all respects similar to that of the so-called basic sulphates except that the precipitation does not occur in even apparent stages, but takes place with every addition of water until complete.

Analyses of these basic precipitates were made showing variable composition. When freshly prepared they showed a ratio of about 10: 1 but this ratio was increased by washing with water, although the acid component washes out much less readily than was previously found to be the case with the corresponding sulphates.

As with the basic sulphates it was early apparent that the precipitates could not be completely separated from the mother-liquors for the purposes of analysis and that it was by no means certain that a single basic salt or two different salts might not be present which were themselves decomposable by water. Fortunately, the question can be settled by phase rule considerations, and the conditions of its applicability to such problems as the identification of individuals in a mixture of basic salts with mother-liquor have been most clearly pointed out by Miller and Kendrick.[1]

In this case we have a system consisting of three components, and if these have arrived at equilibrium at a fixed temperature, the chances of having more than three phases (not considering the gaseous phase) are negligible. Thus in a series of experiments, if the mother-liquors have a constant concentration while the precipitates vary in composition when equilibrium is reached, then

[1] Trans. Roy. Soc. Canada, 7, III, 35.

the precipitate is a mixture of two solid phases. If the mother-liquors vary in concentration while the precipitates have the same composition, then the precipitate is a single chemical compound. If the precipitates and mother-liquors both vary in composition then the precipitate is a "solid solution," *i. e.*, a single homogeneous solid phase of variable composition.

In order to study this question a series of experiments was carried out in the same large and especially constructed thermostat that had been used by one of us upon basic beryllium sulphate. The experiment began on April 13, 1905, and equilibrium was not reached until June 10th. The bottles were continuously agitated throughout this time at a temperature of 25°, being stopped only to remove samples of the mother-liquor for analysis.

The ratio of BeO to C_2O_3 taken is shown in the first column. The amounts taken and the composition of the mother-liquors are shown as indicated.

	Taken.				Found.		
No.	Ratio $BeO:C_2O_3$.	Grams BeO.	Grams C_2O_3.	Grams H_2O.	Gram BeO in 10 grams mother-liquors.	Gram C_2O_3 in 10 grams mother-liquors.	Gram BeO. / Gram C_2O_3 in mother-liquors.
1	2 : 1	0.6972	1	50	No solid phase		
2	2 : 1	1.0458	1.5	50	at this dilution and		
3	2 : 1	0.6972	1	100	temperature.		
4	2 : 1	1.0458	1.5	100	0.0958	0.1501	0.64+
5	2½ : 1	0.8715	1	50	0.1108	0.1847	0.60
6	2½ : 1	1.3073	1.5	50	0.1765	.....	.....
7	2½ : 1	1.7430	2	50	0.2254	0.3818	0.59
8	2½ : 1	0.8715	1	100	0.0567	0.0969	0.58
9	2½ : 1	1.3073	1.5	100	0.0867	0.1466	0.59
10	2½ : 1	2.1788	2.5	100	0.1302	0.2361	0.55
11	3 : 1	1.0458	1	75	0.0750	0.1243	0.60
12	3 : 1	1.5687	1.5	75	0.1228	0.2000	0.61
13	3 : 1	2.0916	2	75	0.1598	.....	.....
14	3 : 1	1.0458	1	100	0.0562	0.0969	0.58
15	3 : 1	1.5687	1.5	100	0.0887	0.1460	0.61
16	3 : 1	1.8302	1.75	100	0.0901	0.1529	0.59
17	4 : 1	1.3944	1	75	0.0667	0.1257	0.53
18	4 : 1	2.0916	1.5	75	0.0953	0.1793	0.53
19	4 : 1	1.3944	1	100	0.0480	0.0935	0.51
20	4 : 1	2.0916	1.5	100	0.0787	0.1465	0.54
21	6 : 1	2.0916	1	75	0.0505	0.1180	0.43
23	6 : 1	2.0916	1	100	0.0390	0.0916	0.43

In examining these figures it should be remembered that ratios between 1.5:1 and 1:1 BeO could not be used, for they give no coexistent solid and liquid phase at any concentration.

A study of the above figures will show at once that the concentrations of the mother-liquors vary widely and therefore the precipitate can not consist of a mixture of two definite basic salts. It will also be evident that the concentration of the mother-liquors is almost exactly proportional to the initial concentration, which shows, as does also the ratio of base to acid, that at these dilutions and at 25° there was little additional precipitation by the dilution from 50 to 100 cc. By comparing Nos. 8, 14, 19 and 23; 11, 17 and 21; and 4, 9, 15, 20 it will also be evident that the composition of the mother-liquors depends almost solely upon the initial concentration of the acid component and is nearly independent of the basic, although a relatively large increase of the initial basic component does diminish the basic ratio in the mother-liquors. It will also be observed that almost all of the acid was left in solution while an increasingly large proportion of the base was thrown out into the precipitate, leaving in most of these experiments a solution of approximately 1.7 BeO:1 C_2O_3. These facts are all in harmony with the conclusion that the solid phase was the hydroxide and that no basic salt exists.

It was early apparent that, as with the basic sulphates, the errors of analysis of the liquid phase would be so multiplied in the calculation as to render any computation of the composition of the solid phase next to useless. It may be well to note, however, that such calculations give in every instance results showing a much higher basicity than those obtained by analysis, which is exactly as would be expected when it is considered that in no case was the precipitate completely separated from the mother-liquors. The precipitates were washed once with water, pressed between filter-paper, dried and analyzed. The results obtained on thirteen of these precipitates follow. The others were not obtained in sufficient quantity for accurate work except Nos. 9 and 10, which were lost through an error and not enough remained for a second determination.

SOLID PHASE.

No.	BeO. Per cent.	C_2O_3. Per cent.	Ratio BeO/C_2O_3.
8	53.2	6.2	23
11	49.7	5.5	26
12	47.8	6.5	21
13	46.3	5.1	26
14	50.6	4.4	34
15	50.1	5.3	27
16	53.2	7.0	22
17	50.5	6.0	26
18	48.3	6.3	22
19	49.6	6.4	22
20	51.2	5.6	26
21	51.0	5.2	28
23	52.8	4.2	35

It will be seen at once that all of these precipitates contain notable quantities of oxalic acid, but from the analysis of the solutions we must conclude that this is probably present in the form of occluded mother-liquors. This is further supported by the fact that the water present was more than sufficient in every instance for the formation of the hydroxide. The presence of this mother-liquor whether great or small in amount gives, of necessity, a resultant solid less basic than the original solid phase. The results themselves taken literally lead to formulas varying from $20Be(OH)_2.BeC_2O_4$ to $34Be(OH)_2.BeC_2O_4$ with a slight excess of water in each case. The analyses are, however, subject to error and a slight error evidently has large effect in the calculation of such highly basic formulas. The possibility of the presence of two definite basic salts having been eliminated by the variation in concentration of the solutions, two propositions alone remain to us. First, that the precipitates are a single solid phase of definite composition which would prove the presence of the simple hydroxide, or a basic salt of a basicity of at least 25BeO to 1 C_2O_3, or that the precipitates vary in composition and, therefore, are solid solutions containing a small amount of the oxalate in the hydroxide. In view of the well-known property of hydroxides to carry down other substances with them when precipitated and the utter improbability of any molecule of so large a ratio of base to acid, the latter conclusion seems justifiable.

"SO-CALLED" BASIC BERYLLIUM COMPOUNDS.

We have tried in the preceding pages to point out clearly that no basic oxalate or basic sulphate of beryllium has ever been

made, and that the indefinite mixtures which have been considered as such were in reality only solid solutions in the hydroxide, and that the two substances mix, as water and alcohol, in all proportions to form a homogeneous solid phase. From a study of the action of other acids on beryllium hydroxide; from the action of water on the truly basic acetate of Urbain and Lacombe and the formate, butyrate, valerate, etc., of Lacombe; and from a careful examination of the original articles cited below we feel confident in the claim that no basic compound of beryllium has been made or probably ever will be made where water is one of the constituents of the system or at least where water is present in sufficient amount to have its mass worthy of consideration in the mass of the system. It can be safely stated that no efforts to make definite salts of beryllium will be successful where attempts are made to saturate an acid with beryllium hydroxide and it is by that method that many of the formulas assigned to so-called compounds of beryllium have been attained.

Among the compounds generally assigned to beryllium the following, in our opinion, have no place and are probably simply solid solutions of the normal salt in the hydroxide.

Basic sulphates and oxalates as cited above.

Basic sulphites:

$2BeSO_3.9Be(OH)_2.6H_2O$;[1]
$BeSO_3.Be(OH)_2+5H_2O$;[2]
$BeSO_3.Be(OH)_2+Aq$;[3]
$3BeSO_3.Be(OH)_2+Aq$.[3]

Basic dithionate:

$2BeS_2O_6.3Be(OH)_2+14H_2O$.[4]

Basic carbonates:

$BeCO_3.5Be(OH)_2+3H_2O$;[5]
$BeCO_3.2Be(OH)_2+Aq$;[6]
$BeCO_3.2Be(OH)_2+3H_2O$;[7]

[1] Seubert and Elten: Z. anorg. Chem. 4, 52.
[2] Atterberg: K. Svenska Vet. Akad. Handl. 12, 51 (1873).
[3] Krüss and Moraht: Annalen, 260, 161.
[4] Krüss: Ann. 246, 195.
[5] Seubert and Elten: Loc. cit.
[6] Parkman: Am. J. Sci. [2], 34, 326.
[7] Debray: Ann. chim. phys. [3], 44, 1.

$4BeCO_3.8Be(OH)_2+5H_2O$;[1]
$2BeCO_3.7Be(OH)_2+3H_2O$;[1]
$2BeCO_3.7Be(OH)_2+2H_2O$.[2]

Basic chlorides:

$3BeCl_2.2Be(OH)_2$;[3]
$BeCl_2.3Be(OH)_2$,[3]
$BeCl_2.12Be(OH)_2+10H_2O$;[3]
$BeCl_2.12Be(OH)_2+4H_2O$;[3]
$Be(OH)Cl$.[3]

Basic selenites:

$2BeSeO_3.Be(OH)_2+2H_2O$;[3]
$BeSeO_3.Be(OH)_2.H_2O$;[3]
$2BeSeO_3.3Be(OH)_2.7H_2O$.[4]

Basic borates:

$Be(BO_3)_2.2Be(OH)_2+Aq$.[5]

Basic nitrate:

$Be(NO_3)_2.Be(OH)_2.2H_2O$.[6]

Basic chromate:

$BeCrO_4.13Be(OH)_2+10H_2O$.[7]

Basic molybdate:

$BeMoO_4.Be(OH)_2.2H_2O$.[7]

Basic succinate:

$BeC_4H_4O_4.Be(OH)_2+2H_2O$.[7]

Basic ferrocyanide:

$Be_2FeCy_6.4Be(OH)_2+7H_2O$.[7]

Basic beryllium hypophosphites,[8] valerates,[9] oxalates, citrates, tartrates, acetates,[10] to which no formulas were assigned nor analyses made.

On the other hand, it must not be forgotten that the truly basic and beautifully crystalline series of salts of the general formula $Be_4O(Ac)_6$, in which the acid constitutent is the radical of formic

[1] Weeren: Ann. Physik. **92**, 91. Weeren seems to have clearly understood that these were no true compounds.

[2] Schaffgotsch: Ann. Physik. **50**, 183.

[3] Atterberg: Loc. cit.

[4] Nilson: Bull. soc. chim. [2], **23**, 355.

[5] Krüss and Moraht: Ann. **260**, 161.

[6] Ordway: Amer. J. Sci. [2], **26**, 197.

[7] Atterberg: Loc. cit.

[8] Rose: Ann. Physik. **12**, 86.

[9] Trommsdorff: Ann. Pharm. **6**, 194.

[10] Vauquelin: Allgem. J. Chem. **1**, 590.

acid or one of its homologues are among some of the most interesting compounds of inorganic chemistry for, although basic in composition, they are all crystallized from anhydrous acid.[1]

CONCLUSIONS.

The following conclusions seem warranted for the ranges of temperature covered by our experiments:

That the only definite hydrated oxalates are $BeC_2O_4.3H_2O$ and $BeC_2O_4.H_2O$.

That no acid oxalate of beryllium exists.

That the anhydrous oxalate BeC_2O_4 is difficult, if not impossible to produce, owing to the difficulty of removing the last trace of water without at the same time decomposing the oxalate.

That the so-called basic oxalates of beryllium do not exist as separate and definite chemical compounds but are in reality solid solutions of the oxalate in the hydroxide. They are much more basic in composition when equilibrium with the mother-liquors is reached than when first precipitated.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 10.]

AN ELEMENTARY PROOF OF THE RELATION BETWEEN THE VAPOR PRESSURES AND THE COMPOSITION OF A BINARY MIXTURE.

BY GILBERT NEWTON LEWIS.

Received February 17, 1906.

BOTH partial vapor pressures from a mixture of two liquids are changed by a change in the composition of the mixture, but not independently. As one decreases, the other invariably increases according to the simple law discovered by Duhem,[2] namely,

$$N\frac{dp}{p}+N'\frac{dp'}{p'}=0,$$

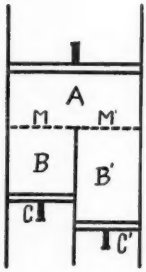
where p and p' are the respective partial vapor pressures from a mixture containing N gram-molecules of the first substance and N′ gram-molecules of the second, and dp and dp' are the changes in p and p' accompanying a slight change in composition.

No satisfactory elementary proof of this very important equa-

[1] Urbain and Lacombe: Compt. rend. 133, 874; Lacombe: Ibid. 134, 772.

[2] Compt. rend. 102, 1449 (1887).

tion has been given. That used by Duhem is rigorous but not elementary, that of Luther[1] is simpler but not entirely rigorous or convincing. I believe that the following proof not only has the advantage of extreme simplicity, but is entirely rigorous and shows clearly the conditions under which the equation is valid.



In the apparatus shown in the figure, A contains a mixture of the substances X and X′. M is a membrane permeable only to the vapor of X, M′ a similar membrane permeable only to the vapor of X′. B contains the pure vapor of X, B′ the pure vapor of X′.

The partial vapor pressures from a mixture of N gram-molecules of X, and N′ gram-molecules of X′, will be designated by p and p' respectively, those from a mixture of N gram-molecules of X and N′—dN' gram-molecules of X′ by $p+dp$ and $p'+dp'$ (dp being numerically positive, dp' negative).

Let us start with a mixture in A of N gram-molecules of X and N′ gram-molecules of X′, and with no vapor in B and B′, the pistons C and C′ being at M and M′. Let us perform the following reversible cycle of *isothermal* operations, *keeping the pressure in* A *constant.*

(1) Keeping the pressures in B and B′ equal to p and p', respectively, lower the pistons C and C′ at such rates that as the mixture in A evaporates, the remainder still has the original composition. Finally, when all the mixture has evaporated there will be N gram-molecules of vapor of X in B, and N′ gram-molecules of vapor of X′ in B′. The pressures of the two vapors will still be p and p'; their volumes we will call V and V′.

(2) By simultaneous movements of the pistons C and C′ change the vapor pressures in B and B′ to $p+dp$ and $p'+dp'$, dp and dp' being defined as above. The corresponding increments of volume we will call dV and dV'. The vapors are now able to exist in equilibrium not with the original mixture, but with a mixture containing X and X′ in the proportion of N gram-molecules to N′—dN'.

(3) Form a mixture of this composition in A by raising the pistons C and C′. This operation will be just the reverse of (1),

[1] Ostwald's Lehrbuch (2) 2, 639 (2d ed.).

except that the vapors enter the mixture in the constant proportion, not of N to N′, but of N to N′—dN'. At the end of this operation all of the vapor of X and all but dN' gram-molecules of X′ will have passed into the mixture.

(4) Finally, force into A the remaining dN' of X′, whereby the vapor pressures of the mixture will return to p and p', and the whole system to its original condition.

During this reversible isothermal cycle the sum of the work done upon the piston in A and the work done upon the pistons C and C′ will be zero. Of these the former is itself equal to zero, for the pressure in A remains constant and the original volume is the same as the final volume. Hence, the total work done upon the pistons C and C′ must equal zero. Let us find the work done upon these two pistons in each of the four operations described, *assuming that the vapors obey the gas law.*

Operation (1) gives,

$$A_1 = -pV - p'V' = -NRT - N'RT.$$

Operation (2), neglecting differentials of the second order, gives,

$$A_2 = -pdV - p'dV'.$$

From the gas law,

$$-pdV = Vdp = \frac{NRT}{p}dp.$$

Hence,

$$A_2 = \frac{NRT}{p}dp + \frac{N'RT}{p'}dp'.$$

Operation (3) gives

$$A_3 = NRT + (N' - dN')RT.$$

Operation (4), neglecting differentials of the second order, gives

$$A_4 = (dN')RT.$$

We have shown that

$$A_1 + A_2 + A_3 + A_4 = 0.$$

We see by inspection that,

$$A_1 + A_3 + A_4 = 0.$$

Hence,

$$A_2 = 0,$$

and

$$N\frac{dp}{p} + N'\frac{dp'}{p'} = 0.$$

In precisely the same way we can show that for a mixture of more than two constituents,

$$N\frac{dp}{p}+N'\frac{dp'}{p'}+N''\frac{dp''}{p''}+\text{----}=0.$$

These equations are true when both the temperature and the pressure of the mixture are constant, and when the vapors behave like perfect gases. As a matter of fact the latter condition is never exactly fulfilled, and the equations must therefore be regarded only as approximations to the truth. How these approximate equations may be replaced by exact equations of similar form will be shown in another place.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 114.]

THE COMBINATION OF A SOLVENT WITH THE IONS.

BY J. LIVINGSTON R. MORGAN AND C. W. KANOLT.

Received March 8, 1906.

I. INTRODUCTION.

THE possibility of the combination of the ions of an electrolyte with the solvent has been suggested by several investigators. Ciamician[1] suggested that the attraction between the solvent and the positive and negative parts of the salt is actually the cause of dissociation. This idea receives support in the fact that the solvents that ionize salts largely are the ones that combine with them to the greatest extent, forming compounds with water of crystallization, alcohol of crystallization, etc.; but the mere fact that such compounds separate out in the solid state is not positive evidence that they exist in the solution.

In this connection it is interesting to note that few of the salts, whose ions are both univalent, separate with water of crystallization, while those with ions of higher valency almost all do. From this we might suspect that univalent ions are less hydrated than bivalent or trivalent ones, and this view is supported by the comparison of the velocities of the ions of different valencies. If we calculate the absolute velocities with which the ions move when subjected to the same force (not the same potential gradient for all

[1] Z. physik. Chem. 6, 403 (1890).

ions, but the same potential gradient for univalent ions, half of this for divalent ions, etc.), we find that in almost all cases monovalent ions move faster than bivalent, and bivalent faster than trivalent. It is to be expected that ions carrying molecules of solvent along with them will meet with greater resistance, and therefore move slower. But here again the evidence is far from being conclusive.

Recently, several methods have been used to show that electrolytes combine with the solvents, but there has been very little evidence obtained that the ions of the electrolytes so combine. There are difficulties in the use of the boiling-point and freezing-point methods in this case, for the effect of a dissolved substance upon the boiling-point or freezing-point of a solvent depends approximately upon the ratio of the number of particles of the dissolved substance to the number of molecules of the solvent. If the solute combines with the solvent the number of molecules of the solute is not changed, but only their size, and the only effect is that due to the removal of a small amount of the solvent from the field. In the case of the dilute solutions, this effect is very slight, but in very concentrated solutions, it becomes appreciable. Jones and his coworkers have made extensive use of this method and have concluded that a considerable number of substances combine with water in solution, and others with alcohol. The results, however, do not show conclusively whether it is the free ions that are so combined, and it can not be considered entirely certain that the observed variations of the boiling-points and freezing-points from the theoretical values are due to hydration and not to something else.

If instead of finding the boiling-point or freezing-point of the solution of a salt in water, we dissolve the hydrated salt in a second solvent and observe the effect on the boiling-point or freezing-point of this solvent, we can determine whether the water of crystallization still remains attached to the salt. Lobry de Bruyn and Jungius[1], and Bruni and Manuelli[2] have used this method and have found evidence of hydration in some cases.

A quantitative determination of the change in the color of a salt solution with dilution is capable of giving some evidence regarding hydration.[3]

[1] Kon. Akad. Amsterdam, June 27, 1903, p. 91.

[2] Z. Elektrochem. 10, 601 (1904).

[3] See Lewis: Z. physik. Chem. 52, 224 (1905).

As the difference of potential between a metal and a solution containing its ions must depend upon the degree of hydration of the ions, a study of such differences of potential might add to our knowledge of hydration, but would alone hardly be conclusive proof of the existence of such hydration.

More direct evidence is to be obtained by observing whether the solvent is carried along by the ions during the electrolysis of a solution. If we simply electrolyze a solution of a salt in water, we cannot tell how much of the change in concentration about the poles is due to the migration of the ions and how much to the water carried by the ions. We might use an apparatus like that of Lodge or that of Whetham, and surround one electrode with a solution containing no water, and observe by some qualitative reaction whether water migrated into this solution, but a suitable qualitative test for water might be hard to find.

Another method that has suggested itself depends upon the probability that hydration diminishes considerably with rise of temperature. If we place our two electrodes in two separate vessels, and connect them by a siphon, and maintain the two vessels at widely different temperatures, the ions passing from the hot vessel to the cold vessel will combine with more water, and those passing in the opposite direction will lose water. Hence we will have a change of concentration at the point of change of temperature, *i. e.*, in the siphon. By making the two vessels sufficiently large, we can eliminate to a large extent the disturbing influence of the change in concentration about the electrodes. The difficulty is that the change of the migration velocities with the temperature would also cause a change of concentration in the siphon, and the amount of this effect would have to be determined.

If we electrolyze a solution of a salt in a mixture of two solvents the combination of the ions with either of the solvents will make itself evident by changes in the ratio of the amounts of the two solvents about the poles. The same result is obtained if, instead of using a second solvent, we use an inert non-electrolyte. Garrard and Oppermann,[1] and Oppermann[2] electrolyzed solutions of various acids, using boric acid as the non-electrolyte. Their results apparently indicated that the hydrogen ions carried water

[1] Nach. Königl. Gesell. Wissen. Göttingen, 56, 86 (1900).

[2] Dissertation, Göttingen, 1901.

with them, but Oppermann suggested that the changes in concentration observed might be due to the negative ions carrying boric acid in the opposite direction; and this explanation becomes very probable when we consider that only one part of boric acid to about fifty parts of water was used. It can easily be shown that the addition of one milligram of boric acid to such a mixture would have fifty times the effect upon the percentage composition that the addition of the same amount of water would. If we had a mixture of fifty parts of boric acid to one of water, the migration of water would have the greater effect upon the composition, and we might disregard the migration of the boric acid; but, of course, boric acid is not sufficiently soluble. Oppermann made another series of experiments with silver acetate as the electrolyte and acetic acid as the non-electrolyte, and the results apparently indicated the hydration of the negative ions; but he used only one part of acetic acid to about twenty-two parts of water, and hence it is more probable that the results were due to the acetic acid being carried in the opposite direction.

Lobry de Bruyn[1] carried out similar experiments with silver nitrate dissolved in mixtures of methyl alcohol and water. Solvents containing 25 per cent., 35 per cent. and 64 per cent. of methyl alcohol were used. He determined the alcohol in each case by distilling a known volume of the solution, and weighing a known volume of the distillate. In this way, he obtained substantially the same weights after electrolysis as before. He neglected, however, the change in volume due to the change in the amount of silver nitrate in the solution, for he found this change in volume to be small. His conclusion was that the results gave no indication of hydration. They certainly do not indicate much hydration; but if he had made corrections for the error mentioned, they would have indicated a slight hydration of the silver ions, which is the result obtained in the present work.

The method used in this work was the same as that used by Oppermann and by Lobry de Bruyn. Silver has great advantages over other metals for this work, because it can be deposited readily from a water solution, and its salts are not hydrolyzed. Some experiments were made with copper nitrate in a mixture of ethyl alcohol and water, but the experiments were abandoned.

[1] Rec. trav. chim. **22**, 430 (1903); Konink. Akad. Wetensch. Amsterdam. Proc. **6**, 97 (1903).

The amount of acid normally present from hydrolysis was increased during electrolysis, and this caused an uncertainty on account of the water taking part in the reaction, and the acid formed was likely to act upon the alcohol. Perhaps some way of overcoming these difficulties is possible, and, if so, the method could be extended to the large class of hydrolyzed salts.

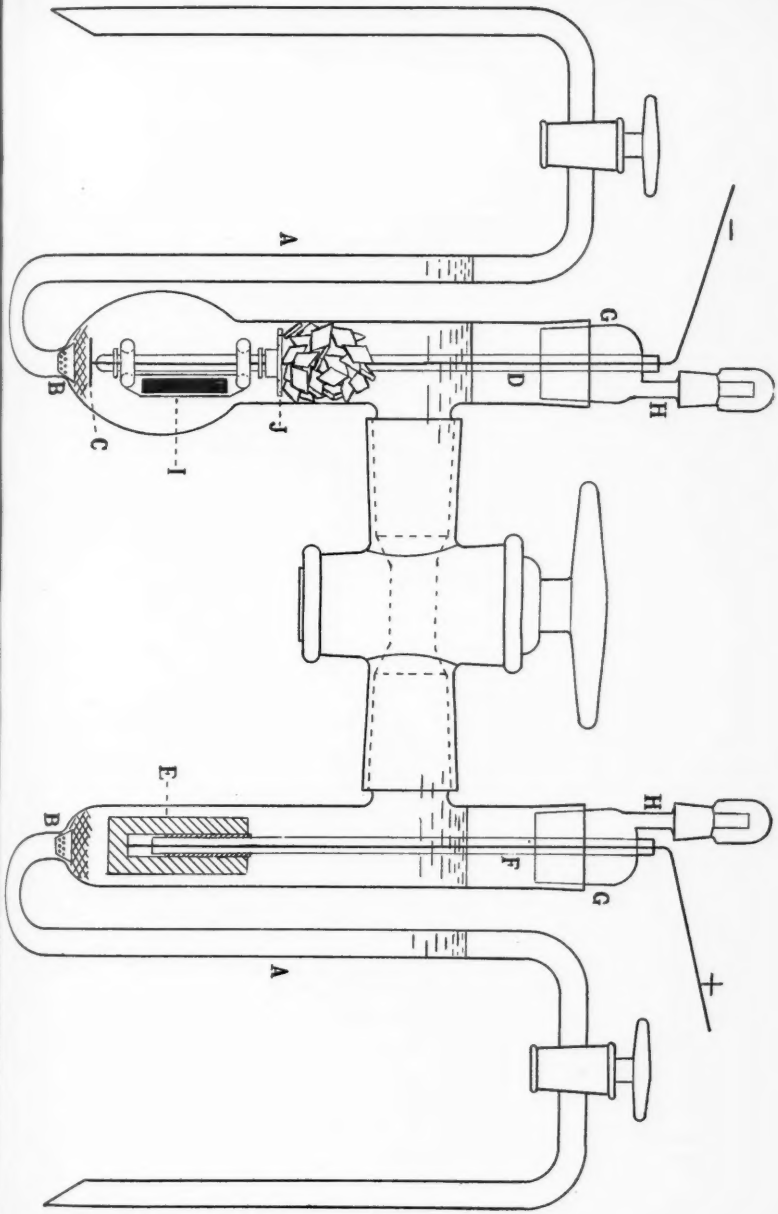
Experiments were made with silver nitrate in a mixture of pyridine and water, with silver nitrate in a mixture of ethyl alcohol and water, and with a mixture of silver nitrate and calcium nitrate in ethyl alcohol and water. The last-named mixture was used with the hope of finding a change of composition too great to be due to silver nitrate alone, in which case it must be due in part to the calcium nitrate. Silver nitrate may crystallize with two and also with three molecules of pyridine of crystallization. That such compounds exist in solution is also indicated by the fact that if a large excess of silver nitrate be added to a dilute aqueous solution of pyridine the solution becomes almost odorless, and no longer gives an alkaline reaction with methyl orange.

II. APPARATUS.

The apparatus used is shown in the figure. It consisted of two vertical tubes of 1.7 cm. internal diameter, connected by a horizontal stop-cock of 1.2 cm. bore. The lower ends of the two vertical tubes bore smaller tubes *A*, *A*, with stop-cocks for the removal of solution. At the junctures of these tubes were perforated platinum cups *B*,*B*, covered with asbestos, to prevent the removal of particles of metallic silver with the solution.

The object of this arrangement was to permit the quantitative removal of the solution from each electrode separately. A known amount of material was put into the apparatus, and the sum of the amounts of each constituent found ought to be the same as the original amount taken. A check was thus obtained upon the results.

The cathode was a platinum disc, *C*, attached to the glass stem *D*. The anode was a cylinder of silver, which is shown in section at *E*. The silver wire by which connection was made with the anode passed through the stem *F*, which extended into a hole bored deep into the anode, and contact was made at the bottom of the hole. The joint between the glass stem and the anode was made tight by a piece of thin rubber tubing. The glass stoppers *G*, *G*, which


A
B
C
D
E
F
G
H
I
J
−
+

bore the electrode stems, also bore the short tubes *H*, *H*, which were closed by ground glass caps.

The stop-cock was connected to the two vertical tubes by ground-glass joints, for it was found that if the apparatus was made in one piece, it was very likely to crack, either during the annealing, or when in use. All ground-glass parts were greased with a mixture of tallow and lard. The amount of this which dissolved in the alcohol was determined in several cases, and was found to be quite negligible.

When certain solutions were used, the silver trees which formed on the cathode grew so rapidly that they would reach the large stop-cock if not prevented. To prevent this without opening the apparatus and thereby allowing evaporation, the device shown at *I* was used. It consisted of a piece of iron within a sealed glass tube so mounted that it could rotate about the electrode stem. When the trees became too high, a large electromagnet was moved about the outside of the apparatus, causing the device within to rotate and break down the trees.

When the more dilute solutions were used, the cathode solution was liable to become very dilute and therefore of high resistance. To prevent this, a weighed amount of dry silver nitrate was placed upon the perforated glass disc *J*, before electrolysis. The use of platinum for such parts is objectionable, for the current is liable to pass through it, causing secondary reactions. Rather large crystals of silver nitrate were used, to avoid great obstruction of the current.

During electrolysis, the apparatus was kept in a tank of water, which was well stirred and kept at a constant temperature. The temperature within the apparatus must have been slightly higher than that of the tank, owing to the heating effect of the current, this effect being different in different parts of the solution.

A mil-ammeter and a silver voltameter were placed in circuit with the apparatus.

In handling the solutions considerable care was necessary to prevent evaporation. The stock solutions were contained in bottles provided with a stop-cock, which was fitted by a ground joint into a tubulure near the bottom of the bottle. To this was attached beyond the stop-cock, by means of another ground joint, a tube bent at right angles, so as to permit this portion of the tube to be cleaned and dried. In filling the apparatus this tube was connected

with one of the tubes *H*, *H*. The air was then exhausted from the apparatus through one of the side tubes, *A*, *A*, and the solution allowed to run into the vacuum. The amount of solution used was found from the increase in the weight of the apparatus. A similar method was used in case a sample of the solution was removed from the bottle to a flask for analysis. In this way all loss of vapor was avoided.

As soon as the electrolysis was finished, the large stop-cock was closed. The solution was then removed from one side of the apparatus by introducing the side-tube *A* into a flask, and blowing into the tube *H*. This side of the apparatus was then washed, and was dried by a current of dry air. The weight of the solution removed was found from the decrease in the weight of the apparatus. The process was then repeated with the other part of the solution, the solution retained in the bore of the stop-cock being allowed to run into the second part. In the case of alcohol solutions, the air displaced from the apparatus and the flask by each portion of wash-water was caused to bubble through cold water, and this water was used for the succeeding washing. Loss of alcohol vapor was thus avoided. This precaution was not considered necessary in the case of pyridine solutions, as the vapor pressure of pyridine from these solutions was so slight that they were almost odorless.

The apparatus was so designed as to offer as little resistance as possible when solutions of high resistance were used, and electrolysis was continued for a rather long time, in order to obtain as great changes of composition as possible. Consequently, a certain amount of mixing of the two solutions undoubtedly occurred, but the aim was to obtain certain evidence of the migration of a solvent rather than an exact determination of the amount of migration. The apparatus was not of the best form for the complete separation of the cathode solution from the anode solution, for there was a tendency for the light cathode solution to circulate through the stop-cock to the upper part of the anode tube. This might have been prevented by making the stop-cock inclined, with the cathode side the higher, or by inclining the whole apparatus during electrolysis.

III. CHEMICALS.

The pyridine used was purified by precipitation as the ferrocyanide according to the method of Mohler.[1] It was then dried by

[1] Ber. 21, 1015 (1888).

potassium hydroxide and distilled. It distilled completely between 115.1° and 115.3° at a barometric pressure of 760 mm. The alcohol was from Kahlbaum, and was redistilled before use. The calcium nitrate was from Kahlbaum. The silver nitrate was Eimer & Amend's C. P.

IV. SILVER NITRATE IN WATER AND ALCOHOL.

In these experiments, silver nitrate, alcohol, and nitric acid were determined directly, and the quantity of water found by difference, the whole of each cathode or anode solution being used for the analysis. A trace of nitric acid was always formed during electrolysis. First, the nitric acid was determined by titration with ammonia solution, with luteol as indicator. The titration was carried on in the flask into which the solution was received from the apparatus, care being taken to avoid loss of alcohol vapor. The alcohol was then distilled off.

A slight modification of the usual procedure in alcohol analysis was adopted. In order to obtain the last trace of alcohol, it is necessary to distil off the greater part of the solution. If the original solution is dilute, this makes the distillate so dilute that the determination of the alcohol content from the density is not as accurate as it might be. In this work a distilling head was used and the distillation conducted slowly until about a third of the solution had distilled off. The density of the distillate was determined. During this distillation the air displaced from the apparatus was caused to bubble through cold water to remove the alcohol vapor. The remainder of the solution was then distilled almost to dryness and the trace of alcohol in this distillate and in the water used to absorb the alcohol vapor from the first, determined by oxidation to acetic acid by the method of Dupré.[1] In the density determinations, a pycnometer of the Ostwald type, capable of giving results with a probable error of less than ±0.00002, was used. The density tables used were those given by Morley,[2] based upon the work of Mendeléeff.

After distillation the silver was determined by precipitation as the chloride.

In several instances tests were made for nitrites and for ammonium salts, since these substances may be formed in the electrolysis of a nitrate solution. Only inconsiderable traces were found.

[1] J. Chem. Soc. 20, 495 (1867).

[2] This Journal, 26, 1185 (1904).

All weighings were corrected for the buoyancy of the air whenever the correction was of the least consequence.

Since the theoretically best conditions for the detection of the combination of the water with the ions are found in a solution containing much less water than alcohol, a solvent was tried which contained 95.36 per cent. of alcohol, and was nearly saturated with silver nitrate. When placed in the apparatus, it was found to have a resistance of about 7,000 ohms, which increased to 20,000 ohms. The increase appeared to be due to the formation of the so-called silver peroxide on the anode. As very little current could be driven through this resistance, the experiment was abandoned. Results were readily obtained, however, with solutions containing less alcohol.

Two analyses were made of the first solution used, with the following results:

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	40.29	40.29	40.29
Silver nitrate	23.73	23.73	23.73
Water	35.98	35.98	35.98

From these results it was found that the solvent contained 52.75 per cent. of alcohol.

Experiment 1.

Temperature: 15°. Amperes: 0.100–0.120. Volts: 73–83. Duration of electrolysis: 8 hours. Silver deposited: 2.9516 grams. Dry silver nitrate used: 4.788 grams. Solution used: 71.795 grams.

In the following table the first two columns give the amounts of the substances found in the cathode and the anode solutions, respectively; the third gives the sums of these; and the fourth gives the amounts present in the original solution, including, in the case of silver nitrate, the amount of the soild material added.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.004	0.002	0.006	0.000
Alcohol	17.413	11.480	28.893	28.926
Silver nitrate	12.801	8.986	21.787	21.825
Water	15.602	10.295	25.897	25.832
Total	45.820	30.763	76.583	76.583
Alcohol in solvent	52.74%	52.76%		52.83%

The following are the results of the analyses of the next solution used:

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	56.50	56.43	56.47
Silver nitrate	14.74	14.74	14.74
Water	28.76	28.83	28.79

The amount of alcohol in the solvent was 66.24 per cent.

Experiment 2.

Temperature: 25°. Amperes: 0.100–0.185. Volts: 110. Duration of electrolysis: 10½ hours. Silver deposited: 6.027 grams. Dry silver nitrate used: 6.439 grams. Solution used: 71.139 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.004	0.002	0.006	0.000
Alcohol	23.603	16.558	40.161	40.172
Silver nitrate	8.311	8.522	16.833	16.925
Water	12.348	8.149	20.497	20.481
Total	44.266	33.231	77.497	77.578
Alcohol in solvent	65.65%	67.02%		66.24%

Experiment 3.

Temperature: 25°. Amperes: 0.10–0.15. Volts: 110. Duration of electrolysis: 9 hours. Silver deposited: 4.394 grams. Dry silver nitrate used: 5.461 grams. Solution used: 69.773 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.015	0.005	0.020	0.000
Alcohol	23.511	15.940	39.451	39.401
Silver nitrate	8.180	7.438	15.618	15.746
Water	12.179	7.909	20.088	20.087
Total	43.885	31.292	75.177	75.234
Alcohol in solvent	65.87%	66.84%		66.24%

It will be seen that in Experiment 1, in which 52.83 per cent. alcohol was used, the composition of the solvent after electrolysis was found to be the same as before, within the experimental error, while in the next two experiments, in which 66.24 percent alcohol was used, there was an appreciable change. This change is in the direction that it would be if the silver ion combined with the water. It is also possible that it was due to the combination of the nitrate ion with the alcohol, but the former explanation is the more probable, for if it were the alcohol that migrated, the change in concentration would be greater in the 52.83 per cent. alcohol than in the 66.24 per cent.

In order to calculate the average number of molecules of water carried by the silver ions, it is necessary to know the relative velocities of the ions in the solvent used. No determinations have been made of the velocities of the ions of silver nitrate in alcohol of the strength used, but if we use the value 0.60 found by Jones and Bassett[1] for the relative velocity of the anion in absolute alcohol, the results will be sufficiently accurate. Using this value, the following results were obtained:

	Total water carried. Gram.	Molecules of water carried by one silver ion.
Expt. 2. Cathode solution.	0.318	0.79
" 2. Anode "	0.290	0.72
" 3. Cathode "	0.196	0.67
" 3. Anode "	0.215	0.73

The numbers are calculated from both the cathode analyses and the anode analyses, independently. We may conclude that the silver ion combines with at least one molecule of water.

It will be seen from the table that there was always a little less silver nitrate found on analysis than was put into the apparatus. This is to be expected, on account of the secondary reaction at the anode in which nitric acid and the so-called silver peroxide are formed. Some water undoubtedly takes part in this reaction, but the amount cannot be great enough to have a considerable effect upon the results; for the greatest loss of silver nitrate, that of 0.128 gram in Experiment 3, is equivalent to only 0.007 gram of water.

V. CALCIUM NITRATE AND SILVER NITRATE IN WATER AND ALCOHOL.

On account of the ready solubility of calcium nitrate in alcohol, it is probable that a solution of good conducting power could have been obtained with very strong alcohol as the solvent, but such experiments would be of little use without results with silver nitrate alone in alcohol of the same strength. Consequently, the work was confined to alcohol of about the same strength as that used with silver nitrate alone.

The calcium was determined, after the removal of the silver, by precipitation as oxalate and ignition to sulphate with sulphuric acid. The whole of the solution was used for the analysis, as before. The other substances were determined as before.

The analyses of the original solution gave the following results:

[1] Am. Ch. J. 32, 438 (1904).

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	49.25	49.31	49.28
Silver nitrate	10.14	10.14	10.14
Calcium nitrate	15.41	15.38	15.39
Water	25.20	25.17	25.19

The amount of alcohol in the solvent was 66.19 per cent.

Experiment 4.

Temperature: 25°. Amperes: 0.140–0.185. Volts: 110. Duration of electrolysis: 7 hours. Silver deposited: 4.632 grams. Dry silver nitrate used: 8.087 grams. Solution used: 78.030 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.008	0.011	0.019	0.000
Alcohol	23.248	15.239	38.487	38.453
Silver nitrate	7.173	8.755	15.928	15.999
Calcium nitrate	7.344	4.688	12.032	12.009
Water	11.972	7.652	19.624	19.656
Total	49.745	36.345	86.090	86.117
Alcohol in solvent	66.01%		66.57%	66.19%

Experiment 5.

Temperature: 25°. Amperes: 0.13–0.18. Volts: 110. Duration of electrolysis: 7½ hours. Silver deposited: 4.781 grams. Dry silver nitrate used: 5.895 grams. Solution used: 74.628 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.003	0.000	0.003	0.000
Alcohol	22.467(?)	14.339	36.806	36.777
Silver nitrate	4.512	8.919	13.431	13.462
Calcium nitrate	7.507	3.964	11.471	11.485
Water	11.509	7.214	18.723	18.709
Total	45.998	34.436	80.434	80.523
Alcohol in solvent	66.13%	66.53%		66.19%

In these experiments there was an appreciable change in the composition of the solvent, but it was so small that it may have been due to the silver nitrate alone, and not to the calcium nitrate. Hence we have no evidence of the hydration of the calcium ion. However, this does not prove that it is not hydrated, for if the calcium ions carried alcohol with them, this might mask the effect of the water carried.

VI. SILVER NITRATE IN PYRIDINE AND WATER.

The stock solution used was made from weighed amounts of material, and was of the following composition:

	Per cent.
Silver nitrate	15.401
Pyridine	3.050
Water	81.549

The amount of pyridine in the solvent was 3.606 per cent.

The solutions to be analyzed were diluted to 250 cc. and 25 cc. taken for each analysis. Two analyses of each solution were made. An excess of hydrochloric acid was added immediately to each sample, to precipitate the silver and convert the pyridine to the hydrochloride, which is less volatile. The silver chloride was filtered out and weighed, and the pyridine determined by the method of François.[1] Pyridine chloraurate, $C_5H_5N,HCl,AuCl_3$, was precipitated by auric chloride, the solution, containing the precipitate, was evaporated to dryness on a water-bath, and the excess of auric chloride washed out with ether. François ignited the precipitate to metallic gold, but in the present work the ether was allowed to evaporate at room temperature, and the precipitate was weighed directly. This method is believed to be preferable, as there appears to be a slight loss when the material is ignited.

Experiment 6.

Temperature: 25°. Amperes: 0.188–0.204. Volts: 30–34. Duration of electrolysis: 6 hours. Silver deposited: 4.663 grams. Dry silver nitrate used: 5.429 grams. Solution used: 72.973 grams.

	Cathode. Grams.	Average cathode. Grams.	Anode. Grams.	Average anode. Grams.	Total found. Grams.	Taken. Grams.
Pyridine	1.477 1.478	1.477	0.696 0.696	0.696	2.173	2.226
Silver	7.263 7.264	7.263	9.321 9.313	9.317	16.580	16.667
Water	....	36.629	....	22.981	59.610	59.509
Total	....	45.369	....	32.994	78.363	78.402
Pyridine in solvent.	....	3.876%	....	2.940%	....	3.606%

Experiment 7.

Temperature: 25°. Amperes: 0.155–0.183. Volts: 37–44.

[1] J. Pharm. Chim. **18**, 337 (1903).

Duration of electrolysis: 5½ hours. Silver deposited: 3.450 grams. Dry silver nitrate used: none. Solution used: 80.792 grams.

	Cathode. Grams.	Average cathode. Grams.	Anode. Grams.	Average anode. Grams.	Total found. Grams.	Taken. Grams.
Pyridine	1.785 1.787	1.786	0.654 0.656	0.655	2.441	2.464
Silver nitrate	5.307 5.308	5.307	7.114 7.116	7.115	12.422	12.443
Water	....	41.607	....	24.324	65.931	65.885
Total	....	48.700	....	32.094	80.794	80.792
Pyridine in solvent	....	4.116%	....	2.622%		3.606

In both these experiments with pyridine, the determinations of pyridine in the same solution have agreed well with each other, but the total amount of pyridine found has been low. This was probably due to evaporation, either of pyridine or of pyridine hydrochloride.

Both experiments give good evidence of the combination of the pyridine with the silver ion. The following table gives the amounts of pyridine carried. The value 0.50 was used for the relative velocity of the cathion of silver nitrate.

	Total pyridine carried. Gram.	Molecules of pyridine carried by one silver ion.
Expt. 6. Cathode solution	0.107	0.063
" 6. Anode "	0.164	0.096
" 7. Cathode "	0.230	0.182
" 7. Anode "	0.255	0.202

In both experiments, needle crystals of $AgNO_3 + 2C_5H_5N$ appeared on the cathode side of the apparatus toward the end of the electrolysis. In the first experiment, they also extended into the top of the anode tube, owing to the circulation of the light cathode solution. In the second experiment, this was largely prevented by inclining the apparatus with the cathode side higher. This accounts for the difference in the results from the two experiments. The amount of the crystals formed was also greater in the second.

The small number of molecules of pyridine carried by the ions does not appear so strange when we consider that the original solution contained only 0.4256 molecule of pyridine to one of silver nitrate. Besides, the number of pyridine molecules available to the ions carrying the current must have diminished as the elec-

trolysis progressed. Hence it is evident that a large proportion of the pyridine in the solution was in combination with the silver ions.

It might be suspected that the migration of the pyridine was due to the electrolysis of pyridine nitrate formed by a secondary reaction at the anode. To produce in this way as great changes as those observed, it would be necessary that nearly or quite all of the pyridine should be in the form of salt. That this was not the case is shown by the fact that the amount of silver nitrate remaining unaccounted for by analysis was not greater in these experiments than in the previous ones, from which it is evident that the extent of the secondary reaction was not greater. As further evidence, an attempt was made to determine the actual amounts of free pyridine in the solutions. The chloraurate method previously used gave both the free pyridine and the pyridine present as salt, in case any salt existed. In order to determine the free pyridine, samples of the solutions were titrated with hydrochloric acid with methyl orange as the indicator. As the silver nitrate would interfere in the titration, the silver was first precipitated as chloride and filtered out. The method is inaccurate, because the end point is not sharp, and a little pyridine is lost by evaporation when the silver chloride is filtered out. The results agreed, however, with those of the chloraurate method, as nearly as the results obtained by the titration of a sample of the original solution agreed with the amount of pyridine known to be contained in it. Hence there could not have been enough pyridine salt present to materially affect the results.

VII. SUMMARY.

(1) When a solution of silver nitrate in a mixture of ethyl alcohol and water was electrolyzed, changes in the composition of the solvent about the poles indicated that water was carried by the silver ion. The results did not indicate the presence of more than one molecule with each silver ion.

(2) It is pointed out that the same conclusion can be drawn from the work of Lobry de Bruyn with silver nitrate dissolved in mixtures of methyl alcohol and water.

(3) When silver nitrate and calcium nitrate were both dissolved in a mixture of ethyl alcohol and water, the changes in the composition of the solvent upon electrolysis were so small that they

may have been due to the hydration of the silver alone, and hence there is no evidence of the hydration of the calcium ions. However, it is not proved that they are not hydrated.

(4) By the electrolysis of a solution of silver nitrate in a mixture of pyridine and water, it was found that a large proportion of the pyridine present was combined with the silver ions.

THE BASIC PROPERTIES OF OXYGEN: ADDITIVE COMPOUNDS OF THE HALOGEN ACIDS AND ORGANIC SUBSTANCES CONTAINING OXYGEN.

BY D MCINTOSH.

Received March 10, 1906.

THE basic properties of oxygen, as exhibited in some organic compounds at low temperatures, have been discussed in a number of articles, and the quadrivalency of oxygen has been suggested to explain the constitutions of the compounds formed. The six principal classes of organic bodies—the alcohols, ethers, ketones, aldehydes, acids and esters—unite with the halogens, and the substances formed have been investigated. Only the first three classes are known with certainty to give compounds with the halogen acids, so that an examination of typical bodies of the last three classes, described in the following pages, may not be without interest.

The halogen acids were prepared in the ordinary way; the aldehyde was made from paraldehyde, the acetic acid purified by several crystallizations, and the ethyl acetate distilled from phosphorus pentoxide.

The compounds were formed with the evolution of large amounts of heat, were crystalline, and had sharp melting-points. They dissolved easily and formed supersaturated solutions in the acid from which they were formed.

Compounds with Hydrochloric Acid.—Aldehyde at —80° C. was quickly changed to paraldehyde by the addition of a few drops of the liquefied acid. The paraldehyde dissolved in an excess of the halogen acid, and a compound melting at —18° separated out on standing. The analyses gave 54.1, 52.4, 53.3 per cent. acid, while $(CH_3CHO)_2(HCl)_3$ contains 55.3 per cent.

Acetic acid gave a product which melted at —53°, and was found to contain 45.7 and 44.5 per cent. of the halogen acid.

$(CH_3COOH)_2(HCl)_3$ requires 47.7 per cent. Ethyl acetate hydrochloride melts at —75° and gave on analysis 47.3 and 46.5 per cent. of acid. Its probable formula is $CH_3COOC_2H_52HCl$, which contains 45.3 per cent. acid.

For comparison, a compound of methyl alcohol and hydrochloric acid was made. It melted at —64°, and contained 46.4 and 44.6 per cent. of acid, while $(CH_3HO)_3(HCl)_2$ contains 43.2 per cent. This product was washed with the liquefied acid, and the high percentage of acid found is due to this.

Compounds with Hydrobromic Acid.—In hydrogen bromide the acetaldehyde was transformed into paraldehyde, which dissolved. A compound melting at —15° and showing on analysis 69.7 and 71.9 per cent. of acid was formed, so that the most likely formula is $(CH_3CHO)_2(HBr)_3$, which requires 73.4 per cent. acid.

Acetic acid does not unite with hydrogen bromide or iodide at low temperatures, but compounds of ethyl acetate and the acids are easily made. The analytical results for the hydrobromic acid product which melted at —40° were: 51.4, 52.0, 52.0 and 52.5 per cent. HBr. $(CH_3COOC_2H_5)_2(HBr)_3$ and $CH_3COOC_2H_5HBr$ contains 58.0 and 47.9 of acid respectively, so that the first formula is to be preferred.

Compounds with Hydriodic Acid.—Paraldehyde and hydriodic acid give a compound melting at —32°. It contained 65.7, 66.4, and 66.0 per cent. acid, while $(CH_3CHO)_3(HI)_2$ contains 66.0 per cent.

The ethyl acetate-hydriodic acid combination melted at —23° and contained 56.3 and 57.1 per cent. acid. Its formula is $CH_3COOC_2H_5HI$, which contains 59.3 per cent.

In the following table are placed the formulas derived from the analytical data given above and the approximate temperatures at which these bodies melt. The ethyl acetate compounds act like those previously described, *i. e.*, the lower the temperature at which they melt, the greater the amount of acid required to "saturate" the oxygen, while the aldehyde compounds vary irregularly. A hydroxyl oxygen atom unites with one, and a ketonic oxygen with two atoms of a halogen. If the oxygen atoms are without influence on each other, we should expect ethyl acetate to unite with three halogen atoms, and this we find to be the case,

[1] J. Chem. Soc. 85, 919 (1904); 85, 1098 (1904); 87, 784 (1905); This Journal, 27, 26 (1905); 27, 1013 (1905).

$CH_3COOC_2H_5Cl_3$ and $CH_3COOC_2H_5Br_3$ being formed. This regularity is not shown in the case of the halogen acid compounds.

COLLECTED RESULTS.

Compounds.	M. P.
$(CH_3HO)_3(HCl)_2$	—64°
$(CH_3CHO)_2(HCl)_3$	—18°
$(CH_3COOH)_2(HCl)_3$	—53°
$(CH_3COOC_2H_5)(HCl)_2$	—75°
$(CH_3CHO)_2(HBr)_3$	—15°
$(CH_3COOC_2H_5)_2(HBr)_3$	—40°
$(CH_3CHO)_3(HI)_2$	—32°
$CH_3COOC_2H_5HI$	—23°

No attempt has been made to indicate the constitutions of these bodies, which may be done by making the oxygen a tetrad. That these compounds differ in many respects from the so-called molecular combinations (salts with water of crystallization etc.), I shall attempt to show in another paper.

MCGILL UNIVERSITY, March, 1906.

THE CONSTITUTION OF CERTAIN NATURAL SILICATES.[1]

BY H. C. MCNEIL.

Received March 6, 1906.

THE representation of natural silicates as substitution products of simple silicic acids, was begun by Professor Clarke about 1886 and has been developed continuously ever since. A formula to be satisfactory is expected to accord with all known facts of the genesis, alterations, artificial syntheses and transformations, as well as physical and chemical properties of the mineral. The chief lines of laboratory work have been fractional analyses by several methods, and varied substitution reactions.

The graphical representations of Butureanu,[2] Vernadsky,[3] and Simmonds,[4] may be mentioned as the more recent attempts in this line.

The present investigation was carried out in the Chemical Laboratory of the United States Geological Survey, under the supervision of Professor Clarke, in the development of his theory

[1] From a thesis submitted for the degree of Doctor of Philosophy, George Washington University, 1905.

[2] Bull. soc. sci. fis. Bucuresci, 1896, 60–73, 117–124, 129–139, 254–279.

[3] Z. Kryst. Min. 34, 37–66 (1901).

[4] J. Chem. Soc. 1903, 1449–1469, and Ibid. 1904, 681–685.

of the constitution of the natural silicates. In one part of the work a simple method was sought for the breaking down of the molecule in fractions, and thus, if possible, to arrive at some conclusions as to its structure. In the second part substitutions within the molecule were studied.

Much of the material used was that already prepared and analyzed in the Survey laboratory. When such material was not available a sample in sufficiently large amount was finely ground and a careful analysis made. The experiments were then carried out on that particular sample. In the first part of the work a sodium carbonate solution, consisting of 100 cc. of water and 25 grams of sodium carbonate, was adopted as one reagent. The experiments were carried out by boiling about a half gram of the prepared mineral in this solution in a covered platinum dish, water being added as it was lost by evaporation. The silica that went into solution was determined by acidifying with hydrochloric acid and evaporating in the usual way. In other experiments 30 cc. of hydrochloric acid consisting of 25 cc. of fully concentrated acid and 5 of water were used. In a covered platinum crucible this would not change bulk appreciably in the longest digestions on the steam-bath. The digestion of the mineral was concluded by evaporating off the hydrochloric acid on the steam-bath. The residue was then treated with hot water, acidified with hydrochloric acid, and the dissolved material determined.

These reagents have been used considerably for the purpose of determining the amounts of silica and alumina liberated under certain conditions, and it was thought that by repeated treatment alternately, some insight into the molecular arrangement might be obtained. The minerals studied were treated with these reagents in a variety of ways and through varying periods of time, in the natural state, after dehydration at low temperatures, and after blasting.

Talc.—A series of twenty-nine experiments was carried out on a sample of talc on the supposition that it was pyrophyllite and rapidly brought to a close when its true nature was determined. The results confirm the observation of Clarke and Schneider[1] that on sharp blasting talc is broken down and yields one-fourth of its silica in a form soluble in a solution of sodium carbonate. The treatment with the sodium carbonate solution must be

[1] Bull. U. S. Geol. Survey, No. 78, 13–15.

rather thorough. Digestion on the steam-bath is not sufficient. Gentle boiling for three hours gave satisfactory results. The part insoluble in sodium carbonate solution is broken down as a whole by the hydrochloric acid used, and not some part of it removed, the effect being so great as to argue against the metasilicate formula for it, that being characterized by great stability toward hydrochloric acid. The results in general are best represented by considering talc to contain an ortho- and a trisilicate radicle, which latter on blasting is transformed into a Si_2O_5 group. This interpretation is in as good accord with alteration data as any other and was proposed as a possibility by Professor Clarke.[1]

Kaolin.—Thirty experiments were carried out on a sample of kaolin from Aikin, S. C., which, according to the analysis of Mr. Steiger,[2] contained 44.94 per cent. SiO_2; 39.18 per cent. Al_2O_3; and 13.85 per cent. water yielded above 100° C.

A half-gram sample boiled with sodium carbonate lost 1.64 per cent. SiO_2. On blasting and treating with the carbonate solution it gave up 2.60 per cent., and when dehydrated at a barely red heat 3.50 per cent. of silica was obtained on three hours' boiling. To the hydrochlroic acid the kaolin lost 2.97 per cent. Al_2O_3. After blasting, only 1 per cent. of Al_2O_3 was obtained on twenty hours' digestion and smaller amounts for a shorter time. On heating barely to redness one hour the loss was 13.51 per cent., and the dehydrated residue yielded 38.79 per cent. Al_2O_3 to the acid reagent.

The effect of sodium carbonate solution on kaolin is small. However, the blasted residue, which by treatment with the acid gave only 1 per cent. of Al_2O_3, lost 7 per cent. of SiO_2 on boiling in the alkali. Similar results were obtained on repetition with other samples. A blasted sample, after treatment with the carbonate solution to which it gave up 1.39 per cent. SiO_2, yielded 8.81 per cent. Al_2O_3 to the acid.

The increase in the amount of material dissolved by one reagent when following a treatment by the other is very noticeable. There is no evidence that the composition of the residue changes, for alumina or silica is in excess, depending on whether the last treatment was with carbonate solution or acid.

Experiments with alumina and freshly prepared silica, mixed

[1] Bull. U. S. Geol. Survey, No. 125.

[2] Ibid. No. 228, p. 355.

and blasted together in the proportion found in kaolin, gave almost no solubility of the silica, and solubility of the alumina almost three times as great as with the kaolin. The formation of $Al_2Si_2O_7$ on igniting kaolin is favored, therefore, rather than the formation of a mixture of Al_2O_3 and SiO_2. The formation of such a compound is easily explained on the supposition that kaolin is an orthosilicate of the constitution proposed by Professor Clarke to accord with its genesis.[1]

$$\begin{matrix} OH \\ Al{-}SiO_2{\equiv}H_3 \\ SiO_2{\equiv}Al \end{matrix} \quad = \quad \begin{matrix} SiO_3 \\ Al \\ SiO_4{\equiv}Al \end{matrix} \quad + \; 2H_2O.$$

Experiment shows that the residue when dehydrated at a low temperature, is completely decomposed by hydrochloric acid, but if blasted, it is but slightly attacked. A possible explanation is that on ignition the residue polymerizes. The explanation of Vernadsky, who assumes that the water in kaolin is held half by the alumina and half by the silica, and only that held by the alumina is driven off at low redness, leaving a partially hydrated molecule decomposable by hydrochloric acid, is proven incorrect, for the kaolin is practically dehydrated at low redness but is almost entirely decomposed by the acid treatment following.

Some experiments of Thugutt[1] have indicated that one-third of the aluminum in kaolin differs from the rest. Indications were found in this work pointing in the same direction, but in an experiment carried out to test this point, the rate of solution runs at a maximum until over one-third of the alumina is dissolved, when there is a decline in the rate, which continues to the end of the experiment, as might be expected if working with a substance of simple constitution. Other experiments bearing on this point fall into line with this observation. All the evidence in this series of experiments favors the formula cited above.

Halloysite.—Halloysite being entirely decomposed by hydrochloric acid, only the product of ignition could be studied by the method used in this investigation. Seven experiments upon a sample from Nevada, nine upon a sample from Texas, and fifteen upon a sample from Kentucky indicate that, on blasting, the compound $Al_2Si_2O_7$ is formed as in the case of kaolin. This

[1] Bull. U. S. Geol. Survey, No. 125, pp. 31–32.

[2] Neues Jahrb. Min., Beilage, Band 9, 592–598.

residue is appreciably more soluble in hydrochloric acid than when derived from kaolin. The formula for kaolin with one added molecule of water satisfies our present knowledge of halloysite. The difference in the effect of acid on kaolin and halloysite may be referred to this water of crystallization, for which there is no adequate theory.

Pyrophyllite.—Seventeen experiments with pyrophyllite showed extreme stability toward the reagents used, though by repeated digestions alternately with acid and alkali it was slowly disintegrated. Blasting had little influence. The carbonate solution showed somewhat greater effect than the acid. Pyrophyllite may be regarded as a true acid metasilicate.

ZEOLITES.

The second part of the work consisted in making substitutions of various metals, using members of the zeolite group for the experiments, as described hereafter. This work follows the same general lines as experiments carried on in the Chemical Laboratory of the Geological Survey for several years by Mr. Steiger, on the same and other minerals. In his experiments sealed tubes have been used, and ammonium, silver, and thallium substitutions, chiefly, were studied. The substitutions herein described were effected by fusion in a platinum crucible at atmospheric pressure.

The formulations were derived by dividing the percentages in the analysis by the molecular weight of the constituent in question, the result thus obtained being used without change.

Analcite.—The material used in these experiments was an analyzed sample from Table Mountain, Colorado, upon which work had already been done by Mr. Steiger. It contained, according to his analysis,[1] SiO_2 55.72 per cent., Al_2O_3 23.06 per cent., Na_2O 12.46 per cent., H_2O 8.39 per cent., and CaO 0.17 per cent. Ignoring the water and combining the monoxide bases, this analcite may be formulated: $R'_{203}Al_{226}Si_{462}O_{1364}$. This may be regarded as made up of a commingling of SiO_4 groups with Si_3O_8 groups in the proportion of 99: 121. Combining these, the formula becomes $R'_{203}Al_{226}X_{220}$, where X stands for the silica radicle in general.

Two grams of analcite and 12 grams of pure barium chloride were fused in a platinum crucible for thirty minutes. An infusible skeleton floated in suspension in the mass. On washing

[1] Bull. U. S. Geol. Survey, No. 207, 11.

the cooled melt, a flocculent residue could be distinguished from a glassy or gritty one. The latter was ground in an agate mortar, washed until barium ceased to be found in the wash-water, dried at 107°, and analyzed.

Analysis A and corresponding formulation derived as with the original analcite.

	Analysis. Per cent.	Formulation.
SiO_2	40.00	$Ba_{261}Al_{356}Si_{622}G_{2039}$.
Al_2O_3	18.16	$SiO_4:Si_3O_8::286:112$.
BaO	40.00	$Ba_{261}Al_{356}X_{398}$.
Na_2O	0.08	
H_2O	1.65	
Total	99.89	

The flocculent material was not in sufficient quantity to furnish a satisfactory analysis.

In succeeding experiments, increasing quantities of barium chloride were used, up to 25 grams. With the increase in the amount of the barium chloride a better fusion was obtained and a lower temperature made possible. The glassy product diminished or disappeared while the flocculent material was much more abundant. A typical analysis of this is given.

	Analysis. Per cent.	Formulation.
SiO_2	45.61	$Ba_{204}Al_{406}Si_{755}O_{2323}$.
Al_2O_3	20.71	$SiO_4:Si_3O_8::230:176$.
BaO	31.36	$Ba_{204}Al_{406}X_{406}$.
Na_2O	Not determined.	
H_2O	1.78	
Total	99.46	

The filtrate from washing the above product yielded 0.2116 gram of silica or 19 per cent. of the total silica in the analcite used, and 0.1042 gram of alumina or 22.6 per cent. of the total alumina.

The first object of the experiments, the substitution of barium for sodium, has been accomplished perfectly. Accompanying this change there has been a breaking down of the analcite to a considerable extent, as shown by the variations in the formulas and the change in the proportions of SiO_4 to Si_3O_8. The silica and alumina thus liberated are dissolved by the barium chloride in somewhat near the same proportions, apparently, so that their presence, while rendering the results less concordant than is to be

desired, does not obscure the general similarity of the barium product to the original analcite, as shown by the approximation to the proportion Ba:Al:X as 1:2:2 in the general formulas, corresponding to R′:Al:X as 2:2:2 in analcite. Since the products of substitution are readily decomposed by hydrochloric acid, and to some extent by the carbonate solution, it is not possible to remove the freed alumina and silica and thus have a pure residue for analysis. The glassy and flocculent products show that we are dealing with mixtures, also.

To test the solubility of silica in fused barium chloride, a gram of freshly prepared silica was blasted and subjected to treatment with fused barium chloride for thirty minutes. On cooling and digesting with water, 9.73 per cent. of the silica was found in the filtrate.

A repetition with 10 grams of barium chloride yielded 9.45 per cent. of silica. With powdered quartz in 10 grams of barium chloride 7.71 per cent. was dissolved. When only 10 grams of barium chloride were used, the addition of the silica necessitated an increase of the temperature almost to the limit of the blast-lamp to keep the mass in a state of fusion. The residue was glassy but on digestion in water it left behind pure silica, the clear filtrates yielding the amounts above stated.

Alumina is not soluble in fused barium chloride, even the air-dried hydroxide, unignited, failing to give results. But the moist hydroxide made from metallic aluminum in sufficient amount to equal 1 gram of alumina, mixed with 10 grams of barium chloride and slowly heated to fusion and so maintained for thirty minutes, gave 11.15 per cent. of the alumina in the filtrate. This unexpected solubility of silica and alumina deserves further investigation.

Where large amounts of barium chloride were used in the analcite experiments perhaps the silica liberated in the destruction of the molecule was largely dissolved, and the alumina only a little less so. In the preparation of the products such as analyzed in A the barium chloride was not in sufficient amount to give a good fusion, but the mass remained pasty. The excess of barium in these products may have been caused by mixtures formed under those circumstances. With a large excess of barium chloride and as low a temperature as possible barely to maintain the salt in fusion, it may be possible to obtain pure products, and make the interpretation of the results possible.

Experiments with strontium chloride show that strontium displaces sodium in analcite completely. The accompanying decomposition is even greater than with barium chloride but the residue obtained still shows the same general type.

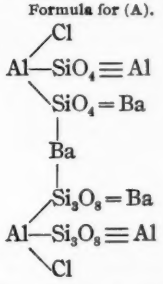
Chabazite.—The chabazite used was a sample from Wassons Bluff, Nova Scotia, used in former experiments in the Survey Chemical Laboratory. The analysis given is by Mr. Steiger:[1] SiO_2, 50.78 per cent.; Al_2O_3, 17.18 per cent.; CaO, 7.84 per cent.; Na_2O, 1.28 per cent.; K_2O, 0.73 per cent.; H_2O, 21.85 per cent.; Fe_2O_3, 0.40 per cent. The formula for this chabazite, if the alkalis are combined, becomes: $R'_{66}Ca_{140}Al_{336}Si_{843}O_{2343}$; combining bases as calcium, $Ca_{173}Al_{336}Si_{843}O_{2343}$; $SiO_4 : Si_3O_8 :: 252 : 86$; $Ca_{173}Al_{336}X_{338}$.

Two grams of chabazite, mixed with 20 grams of barium chloride and the mass kept in quiet fusion as with analcite, gave similar phenomena. The filtrate yielded 20.3 per cent. of the total silica and 11.96 per cent. of the total alumina in the fusion, or $Al_2O_3 : SiO_2 :: 1 : 8\frac{1}{2}$. Analysis B and the formulation are given.

	A. Per cent.	B. Per cent.	Formulation.
SiO_2	40.09	39.68	$Ba_{264}Al_{320}Si_{659}O_{1985}.Cl_{153}$.
Al_2O_3	17.00	16.31	$SiO_4 : Si_3O_8 :: 163 : 171$.
BaO	38.33	40.37	$Ba_{264}Al_{320}X_{334}.Cl_{153}$.
Cl	5.91	5.44	
Less O = Cl	1.63	1.24	
Total	100.00	100.56	

This product is represented by the formula given below, which is of the general chabazite form with chlorine replacing a group $Si_3O_8 \equiv H_2(AlO_2H_2)$, and corresponds to the composition given as the calculated in A. A closer approximation to the analysis could hardly be expected under the circumstances of its production.

Formula for (A).



[1] Bull. U. S. Geol. Survey, No. 207, p. 32.

Another preparation confirmed the above.

The substitution of barium for calcium being found so complete, sodium substitutions were next attempted.

Twenty grams of sodium chloride were fused and 2 grams of chabazite added and kept in fusion thirty minutes. A brisk reaction ensued and a glassy skeleton soon formed that remained unchanged. The product was washed until chlorine-free. No silica or aluminum was found in the filtrate, but 6.70 per cent. of the calcium oxide was obtained, reckoned on the original chabazite. The residue gently ignited gave the following analysis and formula:

	Analysis. Per cent.		Formulation.
SiO_2	55.40		$Na_{558}Ca_{24}Al_{394}Si_{920}O_{2640}.Cl_{188}$.
Al_2O_3	20.16		$SiO_4:Si_3O_8::140:260$.
CaO	1.36		$R'_{606}Al_{394}X_{400}$.
Na_2O	17.33		
Cl	6.69		
Less	1.51	O = Cl.	
Total	99.43		

It is noticeable that with sodium the substitution is not so complete as it is with barium. Using a formula of the same type as for the barium chabazite, and computing the calcium to sodium, this may be represented as a mixture in the proportion of two to one of

$$\begin{matrix} & Cl \\ Al & \\ & Si_3O_8 \equiv Al \\ & Si_3O_8 \equiv Na_3 \end{matrix} \qquad \text{and} \qquad \begin{matrix} & Cl \\ Al & \\ & SiO_4 \equiv Al \\ & SiO_4 \equiv Na_3 \end{matrix} .$$

The composition for this is shown in A and the analysis calculated to 100 per cent. and bases as sodium in B.

	A. Per cent.	B. Per cent.
SiO_2	55.72	55.58
Al_2O_3	20.30	20.24
Na_2O	18.51	18.98
Cl	7.06	6.71
Less O = Cl	1.59	1.52
Total	100.00	100.00

Stilbite.—The sample of stilbite used was from that already prepared and used in experiments carried out recently by Mr. Steiger.[1]

[1] Bull. U. S. Geol. Survey, No. 207, p. 29.

Analysis gives: SiO_2, 55.41 per cent.; Al_2O_3, 16.85 per cent.; CaO, 7.78 per cent.; Na_2O, 1.23 per cent.; and H_2O, 19.01 per cent. Neglecting the water and calculating to 100 per cent. the formulation becomes: $Na_{48}Ca_{170}Al_{410}Si_{1130}O_{3069}$. Combining sodium and calcium gives: $Ca_{194}Al_{410}Si_{1130}O_{3169}$; $SiO_4 : Si_3O_8 :: 44 : 363$; $Ca_{194}Al_{410}X_{407}$.

Twenty grams of sodium chloride and 2 grams of stilbite, fused together, gave exactly the same phenomena as chabazite. Analysis was made on the thoroughly washed mass, which was glassy in appearance. In a repetition of the above experiment the same results were obtained. An analysis is given.

	Analysis. Per cent.	Formulation.
SiO_2	65.58	$Na_{418}Al_{396}Si_{1089}O_{2981}.Cl_{49}$.
Al_2O_3	20.21	$SiO_4 : Si_3O_8 :: 39 : 350$.
CaO	0.79	$Na_{418}Al_{396}X_{389}$.
Na_2O	12.10	
Cl	1.76	
Less O = Cl	0.40	
Total	100.04	

Accounting for the sodium in the same way as in the sodium chabazite, the sodium stilbite may be regarded as a mixture in the proportions of 1 : 1 : 4 of

$$\begin{matrix} & Cl \\ Al & \\ & SiO_4 \equiv Al \end{matrix} \quad \begin{matrix} & Cl \\ Al-SiO_4 \equiv Na_3, & \\ & Si_3O_8 \equiv Al \end{matrix} \quad \begin{matrix} & Cl \\ Al-Si_3O_8 \equiv Na_3, & \\ & Si_3O_8 \equiv Al \end{matrix} \quad \text{and} \quad \begin{matrix} & Si_3O_8 \equiv Na_3 \\ Al-Si_3O_8 \equiv Al. & \\ & Si_3O_8 \equiv Al \end{matrix}$$

The percentage composition of such a mixture is shown in A, and the average of the analyses, calculated to 100 per cent., and the monoxide bases reckoned as Na_2O is shown in B.

	A. Per cent.	B. Per cent.
SiO_2	64.88	65.00
Al_2O_3	20.05	20.03
Na_2O	13.72	13.64
Cl	1.74	1.72
Less O = Cl	0.39	0.39
Total	100.00	100.00

With sodium the substitution is not complete, as it is with barium and strontium, though more nearly so than in chabazite. The breaking down of the mineral is little, however, and the alumina and silica formed by such decomposition, if it occurs,

are not dissolved and removed by the sodium chloride as was the case with the barium and strontium chlorides. The agreement of the analyses with each other and with the theoretical is therefore satisfactory.

Thomsonite.—Like the preceding, the material used was from a sample analyzed and used in similar work by Mr. Steiger.[1] His analysis gives: SiO_2, 41.13 per cent.; Al_2O_3, 29.58 per cent.; CaO, 11.58 per cent.; Na_2O, 5.31 per cent.; H_2O, 13.13 per cent.; total, 100.40 per cent.

Neglecting the water and calculating to 100 per cent. the formulation becomes: $Na_{196}Ca_{230}Al_{664}Si_{783}O_{2890}$. Counting all the bases as sodium it becomes: $Na_{656}Al_{664}Si_{783}O_{2890}$; $SiO_4 : Si_3O_8 :: 602 : 60$; $Na_{656}Al_{664}X_{662}$.

Twenty grams of sodium chloride and 2 grams of thomsonite were fused together, as in the experiments with chabazite and stilbite, with the same results, except that the product of the reaction could not be fused into one mass at the temperature of melted sodium chloride, as was the case with chabazite and stilbite. The product was ground in an agate mortar and washed with great thoroughness. 8.11 per cent. of calcium oxide was found in the wash-water.

A second experiment repeated the first except that the product was ground unusually fine and washed with extreme thoroughness. The results were entirely similar. An analysis and formulation follows.

	Analysis. Per cent.	Formulation.
SiO_2	43.60	$Na_{596}Ca_{50}Al_{650}Si_{724}O_{2729}.Cl_{84}$.
Al_2O_3	33.18	$Na_{696}Al_{650}Si_{724}O_{2729}.Cl_{84}$.
CaO	2.81	$SiO_4 : Si_3O_8 :: 631 : 31$.
Na_2O	18.51	$Na_{696}Al_{650}X_{662}$.
Cl	2.97	
Less O = Cl	0.67	
Total	100.00	

Representing the results with thomsonite on a basis similar to that used for chabazite and stilbite, they may be graphically expressed by

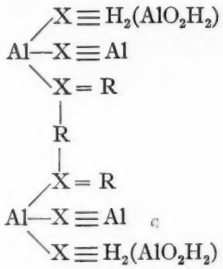
$$4Al\begin{cases}Cl\\Si_3O_8\equiv Al\\Si_4O_8\equiv Na_3\end{cases}, \quad 10Al\begin{cases}Cl\\SiO_4\equiv Al\\SiO_4\equiv Na_3\end{cases}, \text{ and } \quad 25Al\begin{cases}SiO_4\equiv Al\\SiO_4\equiv Al\\SiO_4\equiv Na_3\end{cases},$$

[1] Bull. U. S. Geol. Survey, No. 207, p. 34.

which corresponds to A. The average of the analyses, computed to 100 per cent. and calcium oxide calculated to sodium oxide, is shown in B.

	A. Per cent.	B. Per cent.
SiO_2	43.53	43.76
Al_2O_3	32.02	32.67
Na_2O	22.11	21.26
Cl	3.03	2.98
Less O = Cl	0.69	0.67
Total	100.00	100.00

This formulation best represents the known facts, and places chabazite, stilbite and thomsonite in the same class of zeolites, based on a generalized formula of the type given below, in which X represents chiefly the SiO_4 group in thomsonite, principally Si_3O_8 in stilbite, and a more nearly equal commingling of the two in chabazite.



Generalized formula for thomsonite, stilbite and chabazite.

The results of Mr. Steiger,[1] where silver nitrate or thallium nitrate was used and the N_2O_5 group was retained similarly to the chlorine, admit of the same interpretation as the one used here for the chlorine compounds. Other interpretations are possible for single cases but none found can be applied so generally.

A comparison of this general formula, with that of the chlorine derivative under chabazite, indicates that the basic aluminum is the point of attack for chlorine or N_2O_5. On dehydration, presumably, this aluminum atom has its three valences satisfied by the acid like the other aluminum atoms. Experiments with these zeolites carefully dehydrated before treatment with the fused chloride ought to give valuable results. It is hoped that presently work along this line may be taken up, together with an attempt

[1] Bull. U. S. Geol. Survey, No. 262.

to synthesize by substitutions on kaolin, the sodium-chlorine derivative which is not known. Its relation to kaolin is shown by the formulas:

$$\begin{matrix} & OH & & & Cl \\ & / & & & / \\ Al-SiO_4 \equiv Al & \text{and} & Al-SiO_4 \equiv Al & . \\ & \backslash & & & \backslash \\ & SiO_4 \equiv H_3 & & & SiO_4 \equiv Na_3 \end{matrix}$$

SUMMARY.

A method of fractional analysis has been devised and carried out on four minerals, both with and without previous ignition, in which the material abstracted and the residue left have been studied. This has given some data as to the structure. As a large number of minerals comes to be subjected to this treatment, and as the range of reagents possible to be used is widened, it promises to be a valuable aid in determining constitution.

The work on substitutions has shown that the metals are readily substituted, one for the other, even under the simplest conditions of heating in an open crucible. A type of formula accounting for the retention of chlorine, has been developed for chabazite, stilbite and thomsonite.

Incidentally, the surprising solubility of silica in fused barium chloride and of alumina under certain conditions has been noted and demonstrated.

I wish here to express my heartiest appreciation of the facilities provided, and to acknowledge my great obligation to Professor Clarke for his kindly interest and many invaluable suggestions during the progress of the work.

GEORGE WASHINGTON UNIVERSITY, 1905.

FERRICYANIDES OF MERCURY.

BY GUSTAVE FERNEKES.

Received March 10, 1906.

IN A recent number of this Journal,[1] I described a compound, $K_2HgFe(CN)_6$, which is obtained as a precipitate by the action of mercuric chloride on potassium ferrocyanide. When a solution of potassium ferrocyanide is added to a solution of mercurous nitrate, a precipitate is also obtained. Furthermore, potassium ferricyanide gives precipitates with solutions of both mercuric

[1] This Journal, 28, 87.

and mercurous salts. It is my intention in this paper to show the methods I employed to isolate these precipitates and to ascertain their composition.

Mercuric Ferricyanide, $Hg_3Fe_2(CN)_{12}$.—When an aqueous solution of potassium ferricyanide is added to an aqueous mercuric chloride solution, no precipitate is obtained. The reason for this is that the resulting compound is soluble in water. When, however, a concentrated aqueous solution of potassium ferricyanide is added to a solution of mercuric chloride in alcohol and ether, a heavy yellow precipitate is obtained. This precipitate consists of the compound $Hg_3Fe_2(CN)_{12}$, reprecipitated mercuric chloride and potassium ferricyanide. To remove the mercuric chloride and potassium ferricyanide, one of the two following methods may be employed: The whole precipitate can be transferred to a filter, washed several times with a mixture of alcohol and ether and finally with water. Or the entire precipitate is poured into a measuring cylinder, filled with water. The precipitate is allowed to settle and the supernatant solution removed by means of a siphon. The cylinder is again filled with water, shaken, and the precipitate allowed to settle and the supernatant solution removed as before. This method of washing is repeated four or five times. Finally the precipitate is treated with alcohol and ether, and then filtered and dried at 100° C. The latter method was the one employed for the preparation of the compound, as by this method less loss occurred by solution, and consequently a greater yield of the compound was obtained. The bright yellow compound is fairly stable when in a dry state. It is, however, quite soluble in water and its aqueous solutions decompose rapidly with the evolution of hydrocyanic acid. As a result of this decomposition the solution turns blue with the formation, probably, of Prussian blue. When the dried compound is treated with solutions of alkali hydroxides, the hydroxides of iron and mercury are formed, and the corresponding alkali ferricyanide is again produced. The compound, in its properties, is similar to Turnbull's blue obtained by the action of ferrous chloride upon potassium ferricyanide. It is probably also formed according to the same reaction:

$$3HgCl_2 + 2K_3Fe(CN)_6 = 6KCl + Hg_3Fe_2(CN)_{12}.$$

Numerous analyses performed, as described in my previous paper, gave the following results:

	Found.	Calculated.
Mercury	58.30	58.59
Iron	10.89	10.93
Cyanogen	29.82	30.48
	99.01	100.00

It may be seen that the percentage of cyanogen found is somewhat lower than the calculated percentage. This is due to the fact that a complete decomposition of the compound by boiling with yellow mercuric oxide is not effected. Cyanogen can always be detected in the mercuric oxide, even after boiling the latter with the compound for three hours, and after thorough washing. To attain perfectly accurate results an ultimate analysis by combustion would be necessary. The results are sufficiently accurate, however, to warrant the adoption of the formula $Hg_3Fe_2(CN)_{12}$.

Mercurous Ferricyanide, $Hg_3Fe(CN)_6$.—This compound is obtained as a cream-colored precipitate when a solution of mercurous nitrate is added to a potassium ferricyanide solution. The precipitate is flocculent and can be easily filtered through a Buchner's funnel. It is washed with water and dried at 100° C. The substance invariably turns blue when exposed to the air. From the analyses of this compound, the formula $Hg_3Fe(CN)_6$ is obtained, *i. e.*, three univalent mercury atoms have replaced the potassium in $K_3Fe(CN)_6$.

The results of the analyses are as follows:

	Found.	Calculated.
Mercury	73.70	73.64
Iron	7.02	6.90
Cyanogen	18.91	19.46
Total	99.63	100.00

Again, the percentage of cyanogen is found somewhat lower than the theoretical. In this case, however, a slight decomposition occurred on drying the compound. This decomposition fully accounts for the loss of some of the cyanogen, as correspondingly the percentage of mercury and iron are somewhat high. Finally, an attempt was made to isolate the yellow precipitate obtained by adding a solution of potassium ferrocyanide to mercurous nitrate in dilute nitric acid solution. The compound $Hg_4Fe(CN)_6$ was expected according to the following reaction:

$$4HgNO_3 + K_4Fe(CN)_6 = Hg_4Fe(CN)_6 + 4KNO_3.$$

It was found, however, that the dilute nitric acid oxidized the

ferrocyanide and consequently a homogeneous substance could not be obtained. I then tried to bring about the above reaction by shaking freshly precipitated mercurous chloride with a solution of potassium ferrocyanide, but no reaction took place. The following method, which was tried, might also be mentioned.

Mercurous carbonate was prepared by adding an excess of potassium bicarbonate solution to a mercurous nitrate solution. After a few days the mercurous carbonate is filtered and washed. The greater portion of the precipitate is transferred to an Erlenmeyer flask and acetic acid added in excess. To the turbid liquid obtained, a potassium ferrocyanide solution is added. A heavy precipitate is obtained on shaking, but analyses do not agree with the expected compound of the formula $Hg_4Fe(CN)_6$. The analysis of the substances obtained by the first and last method of preparation approach more closely the formula $Hg_3Fe(CN)_6$, which is the same compound obtained when potassium ferricyanide is added to mercurous nitrate. This seems to show that in the above-mentioned cases oxidation of the ferrocyanide occurred. The preparation of the compound $Hg_4Fe(CN)_6$ will therefore only become possible when a suitable solvent for mercurous chloride is found.

MICHIGAN COLLEGE OF MINES,
HOUGHTON, MICH.,
March 5, 1906.

THE PREPARATION OF BORON CARBIDE IN THE ELECTRIC FURNACE.

BY S. A. TUCKER AND H. J. W. BLISS.

Received March 8, 1906.

THE compound B_6C was first isolated by Joly[1] in some of the products prepared in connection with admantine boron, and Moissan[2] gives three methods for the preparation of the carbide.

(1) An arc is passed between carbon electrodes which are bound together with a mixture of boric oxide and aluminum silicate. Under these conditions the product is contaminated with silicon carbide.

(2) By heating amorphous boron with carbon to a temperature of about 3000° C., either by placing directly in the arc, or by exposing it to the radiant heat from the arc.

[1] Compt. rend. 97, 456.

[2] "Le Four Électrique."

(3) The solution of boron and carbon in certain metals at electric furnace temperatures yields boron carbide, another method which was found by Moissan the most suitable for its preparation.

Further, Mühlhäuser[1] prepared and described a boride of carbon BC, and his method for its preparation consisted in heating a mixture of boric oxide and carbon in an electric furnace. The resulting product consisted of shining black globules of metallic lustre, and, according to the author, scarcely distinguishable from the admixed graphite. After treatment with acids and heating, the product blackened the fingers, but behaved in its action towards reagents similarly to Moissan's carbide.

The purpose of the present investigation was to prepare the carbide in the pure form, using boron oxide as the raw material, and thus to avoid the necessity of using amorphous boron which is obtained with some difficulty and considerable expense.

The first experiments were carried out in the resistance type of electric furnace, constructed entirely of carbon or graphite so as to eliminate the presence of silica. The mixture composed of boric oxide and petroleum coke in molecular proportions was placed about a carbon core or rod raised to a high temperature by the current.

Some metallic-looking globules were thus obtained, but the yield was small and from the fact that the largest portion was found in contact with the carbon rod, it appeared evident that the highest temperatures were necessary for its formation.

The type of furnace was therefore changed to that of the arc, in which one pole was made the graphite crucible composing the body of the furnace while the other consisted of a graphite rod hung vertically through the opening of the crucible. This arrangement enables a powerful arc to be operated in a comparatively small space. For purposes of heat insulation the outside of the crucible was surrounded with a heat-conserving layer such as magnesia. The yield of carbide in such a furnace is decidedly better than in the case of a resistance furnace. The chief difficulty met with was from the volatility of the boric oxide which was to some extent driven off without taking part in the reaction.

Attempts were made to reduce this tendency by the addition

[1] Z. anorg. Chem. 5, 92.

of lime or magnesia, so that these borates might be formed first, but such additions did not improve the yield appreciably.

The method which was finally adopted was to place the petroleum coke in a layer at the bottom of the furnace, and then add the powdered boric oxide through a perforation in the vertical electrode. This, in a large measure, hindered the volatilization of the oxide, as it was thus brought directly in contact with carbon heated to the temperature of the arc.

PHYSICAL AND CHEMICAL PROPERTIES OF THE PRODUCT.

The residual black powder obtained contained no constituent which could be distinguished from the excess of petroleum coke, even under the microscope. The larger globules and the layer found on the core of the resistance furnace resembled fused magnetite, were brittle, easily crushed, and had a brilliant crystalline structure.

In all cases where a layer of the carbide was found attached to the electrode there was also a layer of graphite of fine quality, probably formed by its decomposition. This graphite was very similar to that obtained by the decomposition of silicon carbide. In some cases, however, the boron carbide seemed to melt under the influence of the great heat and thus coat the surface of carbon articles placed in the furnace.

The globules were found to conduct electricity, had a hardness greater than that of silicon carbide and resisted the action of all the usual acids. Fused alkali decomposed it with evolution of carbon monoxide; strong oxidizing agents, such as hot nitric acid with potassium chlorate, and boiling sulphuric acid were without action upon it. The substance is unaffected by heating to redness in the air.

The material obtained from the furnace, consisting of the globules together with other material which appeared to consist of the carbide, was powdered to pass a 30-mesh sieve and then treated after the manner indicated by Moissan, by repeated boiling with nitric acid in conjunction with potassium chlorate, and then with boiling sulphuric acid; in this way the graphite was eliminated and a product of uniform density was obtained which is determined in a liquid separating-column. The compound, after fusion with the alkaline carbonates, was analyzed by Gladding's method.[1] The first lot analyzed gave over 70 per

[1] This Journal, 20, 288.

cent. boron, and was therefore again treated with nitric acid and the chlorate several times. A product was finally obtained which gave, on fusion and analysis, a boron content of 82.8 per cent., allowing for a small undissolved residue, which proved to be carbon.

Since some of this carbon was probably oxidized in the fusion, this result would be a little low. The theoretical boron content of B_6C is 84.6 per cent. Therefore, this analysis together with the general properties of substance identify it with Joly's and Moissan's carbide. The conclusions reached by the foregoing are that Mühlhäuser actually obtained a mixture of the carbide with graphite, owing to the difficulty of separating the latter, but that he failed to obtain any large masses of the product because of the very high temperature necessary.

For the preparation of the carbide from boric oxide in considerable quantities a special form of electric furnace would have to be designed, so that means could be provided for the condensation of the boric oxide fumes—possibly this could be accomplished by using some sort of shaft furnace, whereby these fumes would be retained by the descending charge.

COLUMBIA UNIVERSITY,
NEW YORK.

ALUMINUM PHENOLATE.

BY ALFRED N. COOK.

Received January 16, 1906.

ALUMINUM phenolate was first prepared by Gladstone and Tribe[1] about twenty years ago, but no study was made of the compound except to distil it. While engaged in the study of phenyl ether and its preparation from aluminum phenolate it appeared to the author that a further study of the compound might be interesting and profitable.

Preparation.—The mode of operation found best in its preparation is to heat from 100 to 500 grams of phenol in a liter flask fitted with a return Liebig condenser. A simple air condenser is not sufficient in manufacturing a large quantity, since the escaping hydrogen keeps the tube hot and carries with it a large part of the phenol. In two or three instances in the earlier ex-

[1] J. Chem. Soc. 41, 7.

periments these escaping gases caught fire spontaneously on coming in contact with the air.

The aluminum is added gradually in the form of strips, very slowly at first or the action may be too violent and most of the phenol will escape uncondensed. When the action is well started the heat is removed as the heat of reaction is then sufficient. When the process is thus carried on as far as possible an excess of aluminum strips (which now does no harm) is added and a sharp heat is applied until hydrogen ceases to evolve. It is then poured out on a plate and allowed to cool and bottled up for future use.

A purer product can be obtained by starting with 100 grams than with a larger quantity, since it is subjected to the decomposing action of a high heat for a shorter time and the yield is better. The yield may be made practically quantitive by exercising due care in preventing the loss of phenol.

Gladstone and Tribe found that the action could be started by adding a little iodine, in which case the heat of the water-bath is sufficient, but I have found that 2 or 3 grams of powdered aluminum phenolate will do just as well. It requires a slightly higher heat, however, to start the reaction, probably due to the fact that aluminum phenolate is not dissolved by phenol at the temperature of the water-bath. Endeavors to start the reaction by means of aluminum chloride, and bromine were without success.

A platinum-aluminum couple with phenol as a battery fluid was tested and found to have an electromotive force of 0.1 volt at 54° C., and 0.35 volt at the boiling-point of phenol. The throw of the D'Arsonval galvanometer (which had an internal resistance of 240 ohms) was the same when used alone as when an external resistance of 130,000 ohms was introduced, showing an immense internal resistance.

From the above experiments it was thought that platinum strips might be used to start the reaction. Two experiments were carried out with success, but it required the application of a sharp heat for a few minutes.

Gladstone and Tribe state that aluminum alone is without action on phenol. While this is probably true of pure aluminum I have found that when commercial aluminum and pure phenol are heated sharply for two or three hours a violent reaction sets

up precisely the same as in the other methods. The action was probably produced by local action of a couple of aluminum and carbon, which occurs in aluminum as an impurity.

Analysis.—The analyses for aluminum all yielded high results, probably because the temperature required to complete the reaction of aluminum with phenol is also sufficient to change some of the aluminum phenolate into aluminum oxide and phenyl ether. It was noted that all solvents left a residue undissolved and also that the percentage of aluminum was highest in samples that had been most highly heated during their preparation. It was also observed that some samples, even those that had not been highly heated, had the odor of phenyl ether and when allowed to stand in contact with water for some time this odor was very much intensified.

The aluminum was determined by boiling the substance with water and igniting the resulting hydroxide and also by dissolving in hydrochloric acid and precipitating with ammonium hydroxide.

Calculated for $Al(OC_6H_5)_3$, 8.86 per cent. Found, 9.34 and 9.28 per cent.

In another sample which had been more highly heated at the close, in its preparation, there was found 9.94 per cent. of aluminum in each of two determinations.

Properties.—Aluminum phenolate is a translucent, brittle solid, and possesses a vitreous luster and a conchoidal fracture. When prepared as directed above, it varies from gray to nearly black, and sometimes has the appearance of dried glue. It has a tendency to become brown with age. It has a slight odor of phenyl ether mingled with that of phenol. When bottled up, crystals of phenol sublime and collect on the interior of the bottle in the course of a few weeks. If bottled tightly to exclude the air it may be kept unchanged for many months.

It melts at about 265° C. and when heated a little above the melting-point it begins to decompose as is explained further on. Its specific gravity is 1.23.

Solubility.—The substance is soluble in hot toluene and benzene from which there separates out a gelatinous mass on cooling, which on being dried and analyzed for aluminum yielded results far from that required by theory for aluminum phenolate. There was found 23.85 per cent. Calculated, 8.86 per cent.

It is also soluble in hot xylene but does not separate out on

cooling. On long contact with the air, however, there is gradually deposited a gelatinous mass.

The powdered substance is very readily soluble in methyl, ethyl and amyl alcohol, but not if these contain a little water. A sample of commercial "absolute alcohol" in stock would not dissolve it.

It is soluble in chloroform, carbon disulphide, aniline, carbon tetrachloride, acetone, etc. It is certain that aluminum phenolate reacts chemically with some of these solvents and apparently with all of them. In the case of all of them a very little water causes a large voluminous precipitate immediately, accompanied by the evolution of heat. It is also soluble in a strong solution of sodium phenolate in water. No method was found by which it could be purified.

Action of Water.—When several grams of powdered aluminum phenolate were added to a few cubic centimeters of water considerable heat was evolved. Two experiments were carried out in duplicate to determine the action of water. In the first the phenolate was boiled with water and there was formed $Al_2O_3.2H_2O$, as indicated by the weight of the dried product.

Calculated for $Al_2O_3.2H_2O$, 22.57 per cent. Found, 21.82 and 21.88 per cent.

In the second experiment the phenolate was allowed to remain in contact with cold water for two days when $Al(OH)_3$ was formed.

Calculated for $Al(OH)_3$, 25.39 per cent. Found, 24.30 and 24.29 per cent.

These results are as close as could be expected, considering the purity of the compound, but are sufficient to establish the character of the hydroxide formed. The first is the same hydroxide that is precipitated from a boiling solution of an aluminum salt with ammonium hydroxide, and the second is the same hydroxide that is precipitated from a cold solution of an aluminum salt with the same reagent.

Action of the Air.—When allowed to come in contact with the air for several weeks it loses its vitreous luster and conchoidal fracture and assumes a granular crystalline appearance. It is then moist and smells strongly of phenol, whereas when freshly prepared the odor is comparatively faint. Apparently the moisture of the air acts upon it, liberating phenol and forming aluminum hydroxide, $Al(OH)_3$.

When distilled it does not melt down as fresh aluminum phenolate does, but remains in the granular form in which it was placed in the flask at the beginning. It did not run together in the least and at the close of the operation was poured from the flask as so much sand. From 123 grams of the substance there resulted 89 grams of distillate and 34 grams of powdery residue. It also distilled at a much lower temperature than fresh aluminum phenolate does. On redistilling the distillate about one-third came over in the neighborhood of 100°. This was apparently mostly water but had the characteristic odor of benzene. The temperature then rose rapidly to 179°. About two-thirds came over between 179–180°, the boiling-point of phenol. There were no higher boiling substances formed. The process of distillation evidently simply separated the mechanically held phenol and a little dissolved benzene, and decomposed the aluminum hydroxide, leaving aluminum oxide and other residue. Carbon dioxide does not act upon aluminum phenolate.

Action of Bromine.—Bromine was added to aluminum phenolate in water until all action had ceased. There was immediately precipitated a light yellow compound which, by its melting-point, general properties and the analysis for bromine, was identified as tribromphenol.

When the strong bromine solution had cooled, a golden yellow, glistening compound, finely crystalline, separated out which, by its melting-point, general properties and analysis for bromine, was identified as tribromphenol bromide.

The action of bromine on aluminum phenolate is thus identical with its action on phenol but it acts more smoothly.

Action of Nitric Acid.—When treated with nitric acid aluminum phenolate yields orthonitrophenol, 1-2-4-dinitrophenol, and picric acid, the quantities of each produced depending on the concentration of the acid, the temperature at which it acts, and the time employed. It does not yield metanitrophenol as in the case of phenol, at least not in any considerable quantity. The action is also much milder than in the case of phenol.

Several experiments were carried out as follows: Fifty grams of aluminum phenolate were dissolved in 500 cc. of nitric acid (sp. gr. 1.21) at temperatures varying from —10 to 40°. Practically the same results were obtained each time. On an average there was obtained 20 grams of 2-4-dinitrophenol, 17 grams of nitro-

phenol, and 40 grams of a tarry residue. No picric acid was formed. The two nitrophenols were readily separated from one another and from the tarry residue by distilling under diminished pressure. The orthonitro compound boils at about 120° at 25 mm. pressure and the dinitro compound at 190°.

When aluminum phenolate is dissolved in nitric acid (sp. gr. 1.21) at 60° it is almost completely changed into 2-4-dinitrophenol. A small amount of picric acid is formed at the same time, but no orthonitrophenol. At 100° some dinitrophenol results, but there is formed mostly picric acid, the yield of which is increased on boiling. The dinitrophenol can be completely separated from the picric acid by distilling with steam but the process is long and tedious.

On dissolving aluminum phenolate in commercial nitric acid at the boiling temperature and heating for a short time it was completely transformed into picric acid, no dinitrophenol whatever resulting. If too strong an acid be used, or too great an excess, or if heat be applied too long the yield in picric acid is much reduced, owing to the complete oxidation of part of the compound. In my experiments a given amount of phenol yielded double its weight of picric acid and I think it would be possible to increase the yield still more. The calculated amount is 2.44 times the weight of phenol employed.

The picric acid is obtained in a very pure state. Without crystallization it melted at 120° and after one crystallization from alcohol it melted at 123°, which is the melting-point of the pure compound.

The barium salt of picric acid is described in the literature as containing five molecules of water of crystallization, but in preparing the salt three different times I obtained it with five molecules once, and three molecules twice. The two forms have the same appearance. In each case analyses were made for both barium and water and the results conformed closely to the theoretical.

The barium salt of 2-4-dinitrophenol is described as crystallizing from water with seven, six, and five molecules of water of crystallization. I prepared the yellow salt twice and analyzed it for both barium and water and in both instances it contained but four molecules. The results were in close agreement with the calculated.

The orange-red crystals which are described as containing five molecules of water were also analyzed for both barium and water and found to contain but four. The orange-red crystals on repeated recrystallization change gradually and finally completely into the yellow variety.

Action of Alcohol.—When commercial "absolute alcohol" was treated with powdered aluminum phenolate an action began at once and the temperature rose to a very perceptible degree and there was formed a gelatinous emulsion. The action was at first thought to be due to the presence of water in the alcohol, but some fresh absolute alcohol was prepared by means of calcium carbide from the commercial article (Eimer & Amend), and it was found that the aluminum phenolate dissolved in it very quickly with no perceptible evolution of heat. However, on adding a few cubic centimeters of water a bulky precipitate was thrown down and a marked evolution of heat took place.

The filtrate contained phenol as was shown by well-known tests, although the characteristic odor and caustic action were absent, on account of the presence of the alcohol. On distillation a residue of phenol remained. The precipitate was washed with alcohol and analyzed for aluminum with the following results:

Calculated for $Al(OC_2H_5)_3$: Al, 16.72 per cent. Found: Al, 17.47 and 17.26 per cent.

The alcohol radicle therefore simply takes the place of the phenol and the following equation would represent the reaction:

$$Al(OC_6H_5)_3 + 3HOC_2H_5 = Al(OC_2H_5)_3 + 3HOC_6H_5.$$

Action of Ether.—Powdered aluminum phenolate was treated with commercial ether, when there was obtained a flaky precipitate similar to that yielded by alcohol. Some absolute ether was prepared by means of sodium, from the commercial article. In this it quickly dissolved (with the exception of a small residue, probably Al_2O_3) with no evolution of heat. On adding a few cubic centimeters of water a bulky precipitate was formed immediately, accompanied by a marked evolution of heat. The precipitate was washed with ether and analyzed for aluminum and gave results in fair agreement with the requirement of theory for aluminum alcoholate, considering the conditions under which the compound was obtained. The filtrate was distilled and from it there was obtained a nearly quantitative yield of phenetol and

a small quantity of a high-boiling crystalline solid which was not examined. The following equation would represent the reaction:

$$3C_2H_5OC_2H_5Al(OC_6H_5)_3 = Al(OC_2H_5)_3 + 3C_2H_5OC_6H_5.$$

Action of Other Reagents.—Hydrochloric acid acts upon aluminum phenolate, liberating phenol and precipitating aluminum chloride. Sulphuric acid acts in an analogous manner. Hydrofluoric acid attacks it vigorously with the liberation of phenol. Acetic acid attacks it rather tardily and the weaker organic acids are without action upon it.

A solution of sodium hydroxide dissolves it, probably forming sodium aluminate and sodium phenolate. On adding a strong acid, phenol is liberated.

A strong solution of sodium hypochlorite dissolves it.

Distillation.—On being sharply heated aluminum phenolate melts and very soon begins to decompose. The products of distillation are a small quantity of benzene (which, however, may have resulted from the reducing action of the hydrogen during the process of manufacture and may have been simply held in solution in the solid aluminum phenolate), phenol, a varying amount of phenyl ether, depending upon the amount of heat employed, and some higher boiling substances not easily separated from one another and not identified.

The degree of heat should be as low as possible (and applied with a smoky flame) if it is desired to obtain as large a yield of phenyl ether as possible. There is also obtained by low heating a relatively larger amount of tarry residue. When a high degree of heat is employed the aluminum phenolate decomposes mostly into phenol and the higher boiling substances; much less phenyl ether is formed and there remains much less of the tarry residue. Some aluminum phenolate always passes over in the first distillation but is entirely decomposed during the second. On distilling *in vacuo* much more of the aluminum phenolate passes over unchanged, together with a larger amount of phenol and a very small amount of phenyl ether. From these results one would suspect that a larger yield of phenyl ether might be obtained by distilling under increased pressure, but the experiment was not tried on account of a lack of suitable apparatus.

By heating the flask as uniformly as possible during the whole operation and carrying the distillation as far as possible, a porous

residue remains which can quite readily be removed from the flask; otherwise, a hard asphalt-like residue remains which it is impossible to remove without sacrificing the flask.

As a method of preparing phenyl ether this is no doubt the best that has been employed up to the present unless it be the one recently proposed by Ullmann and Sponagel.[1] I have gone carefully over all of the other methods and find that this gives far the best yield. From 1227 grams of aluminum phenolate I obtained over 200 grams of phenyl ether boiling at 249–251°, by washing the first distillate with a solution of caustic soda to remove the phenol and fractionating the remainder. The caustic soda solution must be quite weak since phenyl ether is quite soluble in a strong solution of sodium phenolate. Having gone over the process a number of times I have calculated that about one-third of the aluminum phenolate is decomposed into aluminum oxide and phenyl ether probably according to the following equation:

$$2Al(OC_6H_5)_3 = Al_2O_3 + 3C_6H_5—O—C_6H_5.$$

From the action of alcohol on aluminum phenolate it was thought that phenyl ether might be the result of the reaction of phenol, but equimolecular quantities of the two substances were heated for more than an hour and on extracting with ether and distilling, no phenyl ether was formed.

I am indebted to Mr. W. J. Morgan, of Iowa City, Ia., for some assistance in part of the work.

The action of aluminum phenolate on various organic compounds is now being studied in this laboratory and will be the subject of a future paper.

NOTE.—Since writing the above an endeavor was made to continue the study of the action of aluminum phenolate on organic compounds with some of the freshly prepared substance, but the solubility and the chemical action were found to be only very slight in every case. Aluminum phenolate was then prepared in a variety of ways from the same lot of chemicals in each case as was used several months ago, but all were without action. The substance used in that part of the research in connection with organic compounds was about a year old. Apparently some change takes place in aluminum phenolate with

[1] Ber. 38, 2211, 1905.

age. A quantity has been prepared and will be kept until a year hence when it is hoped that this study can be resumed.

UNIVERSITY OF SOUTH DAKOTA,
VERMILLION, S. DAK.
December 18, 1905.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. NO. 121.]

ON DIMETHYL 4-AMINOPHTHALATE AND CERTAIN OF ITS ACYL DERIVATIVES.

BY MARSTON TAYLOR BOGERT AND ROEMER REX RENSHAW.

Received January 11, 1906.

AS A sequel to the work on the nitro-*o*-phthalic acids recently conducted in this laboratory,[1] we have turned our attention to the aminophthalic acids also.

Very little information appears in the literature concerning 4-aminophthalic acid or its derivatives. It seemed of interest, therefore, to prepare a number of its derivatives and study their properties.

As the free 4-aminophthalic acid is not readily obtained pure, on account of its instability, we used its dimethyl ester as the starting point for our experiments. This was prepared from phthalic anhydride by nitrating, esterifying the mixture of nitro acids which result, separating the neutral ester of the 4-nitrophthalic acid, and then reducing the nitro acid with alcoholic hydrochloric acid and zinc dust. By this method, the amino ester was obtained in satisfactory yield and purity. Quite lately, Cohen and McCandlish[2] tried to reduce the nitrophthalic ester with hydrogen sulphide, but could get no pure product, the amino ester formed being invariably contaminated with a yellow, viscid oil, which they thought was probably a sulphur compound.

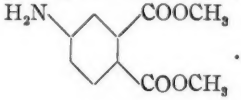
From the dimethyl ester, we prepared the following derivatives: hydrochloride; a dimolecular condensation product with formic acid; acetyl, propionyl, isobutyryl, benzoyl, *m*- and *p*-nitrobenzoyl, urethane, phenyluramino, ethoxalyl, oxalyl, phthalamic acid, succinamic acid, and the silver salts of both the latter; also 4-aminophthalanil.

[1] Bogert and Boroschek: This Journal, 23, 740 (1901); Bogert and Wright: Ibid. 27, 1310 (1905.)

[2] J. Chem. Soc. 88, 1269 (1905).

EXPERIMENTAL PART.

Preparation of Dimethyl 4-Aminophthalate,



—Phthalic anhydride was nitrated as described by Bogert and Boroschek,[1] and the resulting mixture of 3- and 4-nitrophthalic acids partially separated by fractional crystallization. Two hundred grams of the crude 4-nitro acid thus separated were boiled for eight hours with 320 grams of methyl alcohol and 60 grams of concentrated sulphuric acid. The 4-nitro acid is thus changed to the neutral dimethyl ester, while any 3-nitro acid present forms mainly the acid monomethyl ester. The excess of methyl alcohol was evaporated, the residue poured into cold water, the oily ester layer separated and agitated with an excess of sodium carbonate solution. The acid ester is dissolved by this treatment, while the neutral ester remains undissolved as a waxy solid. The crude neutral ester was thoroughly washed with water, and purified by recrystallization from alcohol.

The dimethyl 4-nitrophthalate was reduced by alcoholic hydrochloric acid and zinc dust, as described by Baeyer,[2] Miller,[3] Edinger,[4] Onnertz[5] and others, for the corresponding diethyl ester. Fifty grams of the nitro ester were treated with 250 grams of alcohol and 500 grams of concentrated hydrochloric acid. The mixture was cooled to 0°, stirred with a turbine, and small amounts of zinc dust added from time to time. It is advisable to continue the addition of the zinc dust for some time after all the nitro ester has dissolved, as otherwise the amino ester may be contaminated by intermediate reduction products at the close of the reduction, the solution was diluted with an equal volume of water, filtered from excess of zinc dust, and the greater part of the acid carefully neutralized with sodium hydroxide solution, the temperature being kept down by occasional additions of cracked ice. Final neutralization was accomplished by adding sodium carbonate solution as long as the precipitate which first

[1] Loc. cit.
[2] Ber. 10, 124, 1079 (1877).
[3] Ibid. 11, 1191 (1878).
[4] J. pr. Chem. [2] 53, 375 (1896).
[5] Ber. 34, 3735 (1901).

formed redissolved on stirring. The amino ester was then precipitated by the addition of a saturated solution of sodium acetate, and the mixture left for a few hours in the refrigerator. The amino ester separated in slightly colored glistening plates, which were filtered out, and purified by crystallization from alcohol or benzene. The yield was about 88 per cent. of the theory.

Dimethyl 4-aminophthalate crystallizes from alcohol or benzene in shining white plates; from water, in long hexagonal prisms. It melts at 84° (corr.). It is soluble in cold alcohol, acetone, chloroform, nitrobenzene, aniline, pyridine, or mineral acids; slightly soluble in hot water, carbon tetrachloride or ether; difficultly soluble in carbon disulphide or in petroleum ether.

Calculated for $C_{10}H_{11}O_4N$: C, 57.40; H, 5.30; N, 6.70. Found: C, 57.22; H, 5.26; N, 6.65.

Hydrochloride.—The amino ester was dissolved in dry benzene and treated with benzene saturated with dry hydrogen chloride. A gummy precipitate separated, which soon hardened to a crystalline mass. This was removed, washed with dry benzene, and dried in a vacuum desiccator. It dissolves freely in water, but soon dissociates with precipitation of the free amino ester. In a moist atmosphere, it slowly gives off hydrogen chloride.

ACYL DERIVATIVES OF DIMETHYL 4-AMINOPHTHALATE.

I. Derivatives of the Acetic Acid Series.

Dimethyl 4-Aminophthalate and Glacial Formic Acid.—Five grams of the amino ester were boiled for three hours with an excess of glacial formic acid. The excess of acid was then evaporated, and the residual oily material crystallized from alcoholic formic acid. In this way, a small amount of crystalline product was obtained. The mother-liquors appeared to contain one or two other substances, which, however, were not further investigated.

The substance separated by crystallization from alcoholic formic acid, forms nearly colorless microscopic crystals, m. p. 179° (corr.), which are soluble in alcohol, hot ethyl acetate, acetone, or benzene; very difficultly soluble in ether, carbon disulphide, chloroform or petroleum ether. They are apparently quite easily hydrolyzed.

On analysis, the amount of nitrogen found was 6.66 per cent. This agrees closely with the theoretical amount of nitrogen present in the dimolecular condensation product, $(CH_3OOC)_2$

$C_6H_3NHCH:NC_6H_3(COOCH_3)_2$, resulting from a condensation of the formyl derivative first produced with a second molecule of the amino ester.

Nitrogen calculated for $(CH_3OOC)_2C_6H_3NHCOH$, 5.92; nitrogen calculated for $(CH_3OOC)_2C_6H_3NHCH:NC_6H_3(COOCH_3)_2$, 6.54; nitrogen found, 6.66.

Dimethyl 4-Acetaminophthalate, $C_6H_3(COOCH_3)_2NHCOCH_3$.—Five grams of the amino ester were boiled for some time with an excess of acetic anhydride. The solution was then precipitated by dilution with water, the precipitate filtered out, washed thoroughly with water, and crystallized from 30 per cent. alcohol. It was thus obtained in small, colorless crystalline plates, melting at 136.5° (corr.). It dissolves in alcohol, chloroform, benzene, acetone, hot carbon disulphide, ether, or water, but is very difficultly soluble in petroleum ether.

Calculated for $C_{12}H_{13}O_5N$: N, 5.58. Found: N, 5.76.

Dimethyl 4-Propionaminophthalate, $C_6H_3(COOCH_3)_2NHCOC_2H_5$.—The amino ester was boiled with propionic anhydride, the propionic acid and excess of anhydride distilled off, the residual oil dissolved in alcohol, treated with bone-black, and precipitated by diluting with water and cooling in a freezing-mixture. The substance was thus obtained in crystalline condition. It was recrystallized by dissolving it in benzene and carefully adding petroleum ether.

This propionyl derivative crystallizes in long, thin, colorless needles, melting at 110.5° (corr.); soluble in alcohol, benzene, acetone, ethyl acetate, ether, or chloroform; insoluble in petroleum ether, or cold water.

Calculated for $C_{13}H_{15}O_5N$: N, 5.30. Found: N, 5.5 and 5.59.

Dimethyl 4-Isobutyraminophthalate, $C_6H_3(COOCH_3)_2NHCOCH(CH_3)_2$.—The amino ester was dissolved in just sufficient isobutyric anhydride to effect solution, and the solution was then boiled for an hour. On cooling, a brownish solid resulted. This was pulverized, washed with water, dissolved in alcohol, the solution treated with bone-black and cooled. The crystals which separated were purified by solution in benzene and reprecipitation with petroleum ether, or by recrystallization from dilute alcohol.

The isobutyryl derivative crystallizes in long, thin, colorless needles, melting at 122–123° (corr.), which dissolve in alcohol,

benzene, chloroform, carbon disulphide, ether, or acetone, but are very difficultly soluble in water or petroleum ether.

Calculated for $C_{14}H_{17}O_5N$: N, 5.0. Found: N, 5.16.

II. Derivatives of the Benzoic Acid Series.

Dimethyl 4-Benzoylaminophthalate, $C_6H_3(COOCH_3)_2NHCOC_6H_5$.—The amino ester was dissolved in pyridine, the calculated amount of benzoyl chloride added, and the product precipitated by the addition of water. By crystallization from benzene, it was obtained in colorless needles, melting at 132–132.5° (corr.); soluble in alcohol, benzene, acetone, chloroform, or ethyl acetate; slightly soluble in carbon disulphide; very difficultly soluble in ether, naphtha, or water.

Calculated for $C_{17}H_{15}O_5N$: N, 4.40. Found: N, 4.64.

Dimethyl 4-m-Nitrobenzoylaminophthalate, $C_6H_3(COOCH_3)_2NHCOC_6H_4NO_2(m)$.—The amino ester was dissolved in pyridine, treated with the calculated amount of *m*-nitrobenzoyl chloride, and the mixture heated for some time. The mixture when poured into water separated an oil. This oil was washed free from pyridine hydrochloride, dissolved in alcohol, the solution concentrated to crystals, and the crystals recrystallized from benzene.

The substance forms nearly colorless scales, melting at 147° (corr.).

Calculated for $C_{17}H_{14}O_7N_2$: N, 7.83. Found: N, 7.87.

Dimethyl 4-p-Nitrobenzoylaminophthalate, $C_6H_3(COOCH_3)_2NHCOC_6H_4NO_2(p)$.—This was prepared in the same way as the meta derivative just mentioned. It crystallizes from alcohol in small yellowish flakes, melting at 202° (corr.). It is slightly soluble in cold alcohol, hot amyl acetate, or hot benzene; very difficultly soluble in carbon disulphide, chloroform, or naphtha.

Calculated for $C_{17}H_{14}O_7N_2$: N, 7.83. Found: N, 7.95.

III. Derivatives of Carbonic Acid.

Dimethyl 4-Urethanophthalate, $C_6H_3(COOCH_3)_2NHCOOC_2H_5$.—Three grams of ethyl chlorcarbonate were added to a dilute alcoholic solution containing 4 grams of the amino ester and 2 grams of sodium carbonate. The reaction was accompanied by rise of temperature and evolution of carbon dioxide, and was completed by warming for a few minutes on the steam-bath. On careful dilution with water a precipitate was obtained, which,

recrystallized from boiling water, separated in long needles, melting at 122° (corr.).

This urethane is soluble in alcohol, acetone, ethyl acetate, ether, carbon tetrachloride, chloroform, or hot water; difficultly soluble in cold water, and apparently insoluble in petroleum ether.

Calculated for $C_{13}H_{15}O_6N$: N, 5.0. Found: N, 5.13.

Dimethyl 4-Phenyluraminophthalate, $C_6H_3(COOCH_3)_2NHCONHC_6H_5$.—Five grams of the amino ester, dissolved in dry benzene, were treated with excess of phenyl isocyanate, and the solution gently boiled for two hours. The benzene solution was then concentrated, petroleum ether carefully added, and the solution placed in an ice pack. The crystals thus obtained were purified by recrystallization from benzene.

The pure substance forms microscopic needles, melting at 138° (corr.), which are soluble in alcohol, benzene, ether, acetone, ethyl acetate, or chloroform, but very difficultly soluble in carbon disulphide, or petroleum ether.

Calculated for $C_{17}H_{16}O_5N_2$: N, 8.50. Found: N, 8.64.

IV. Derivatives of Bibasic Acids.

Dimethyl Ethoxalyl-4-aminophthalate, $C_6H_3(COOCH_3)_2NHCOCOOC_2H_5$.—Five grams of the amino ester were heated for several hours with a slight excess of ethyl oxalate. After distilling off the alcohol formed in the reaction, there remained an oil containing a small amount of a white precipitate. On extracting with boiling alcohol, the oil was all dissolved, while the precipitate remained insoluble. On concentrating the alcoholic extracts, the ethoxalyl derivative was precipitated, and it was then purified by recrystallization from alcohol.

As thus prepared, it formed small white flakes, melting at 121.5° (corr.); soluble in alcohol, benzene, acetone, ethyl acetate, ether, chloroform, or carbon tetrachloride; very difficultly soluble in naphtha.

Calculated for $C_{14}H_{15}O_7N$: N, 4.52. Found: N, 4.77 and 4.75.

Dimethyl Oxalyl-4-aminophthalate, $C_6H_3(COOCH_3)_2NHCOCONHC_6H_3(COOCH_3)_2$.—The white insoluble precipitate observed in the foregoing reaction proved to be the corresponding oxalyl derivative resulting from the condensation of the ethoxalyl body with a second molecule of the amino ester. It was purified

by digesting successively with alcohol, benzene, ether, and chloroform.

It is insoluble or very difficultly soluble in alcohol, benzene, ether, chloroform, acetone, ethyl acetate, carbon disulphide, nitrobenzene, petroleum ether, or water, and melts at 239° (corr.).

Calculated for $C_{22}H_{20}O_{10}N_2$: N, 5.9. Found: N, 5.68.

Phthalamic Acid of Dimethyl 4-Aminophthalate, $C_6H_3(COOCH_3)_2NHCOC_6H_4COOH$.—A benzene solution of 5 grams of the amino ester was added to a saturated benzene solution of phthalic anhydride, and the whole boiled until it became decidedly turbid. On concentrating and cooling, microscopic crystals separated in large amount. These crystals were purified by dissolving in amyl acetate and adding petroleum ether, or, better, by dissolving in alcohol and adding benzene. Attempts to crystallize from dilute alcohol resulted in more or less hydrolysis of the compound.

It is soluble in alcohol, acetone, or amyl acetate; slightly soluble in boiling benzene, or in ether; very difficultly soluble in water, chloroform, or petroleum ether. It melts at about 166–167° (corr.) with loss of water, probably passing thereby into the corresponding imide.

Calculated for $C_{18}H_{15}O_7N$: N, 3.93. Found: N, 3.92.

Its *silver salt* was also prepared, by precipitating the solution of the ammonium salt with silver nitrate. Washed with water and dried, it resembles silver chloride in general appearance.

Calculated for $C_{18}H_{14}O_7NAg$: Ag, 23.22. Found: Ag, 23.10.

Succinamic Acid of Dimethyl 4-Aminophthalate, $C_6H_3(COOCH_3)_2NHCOCH_2CH_2COOH$.—This was prepared from the amino ester and succinic anhydride in much the same way as the phthalamic compound. The succinamic derivative separated on concentrating the benzene solution and was purified by crystallization from water.

It crystallizes from water in colorless needles, melting at 173° (corr.), with loss of water and presumably with formation of the imide. It is soluble in boiling water, in alcohol, acetone, or ethyl acetate, slightly soluble in hot benzene, and very difficultly soluble in ether, chloroform, carbon tetrachloride, or naphtha.

Calculated for $C_{14}H_{15}O_7N$: N, 4.5. Found: N, 4.68 and 4.74.

By precipitating a solution of the ammonium salt with silver nitrate, the *silver salt* generally separated in a gelatinous form,

but, on standing in the solution, it gradually changed to a more granular condition.

Calculated for $C_{14}H_{14}O_7NAg$: Ag, 25.94. Found: Ag, 26.06.

4-Aminophthalanil, $H_2NC_6H_3\langle{}^{CO}_{CO}\rangle NC_6H_5$.—

Five grams of dimethyl 4-aminophthalate were dissolved in boiling aniline, and the boiling continued for a short time. An excess of acetic acid was added to the cooled solution and then water. By this dilution the anil was thrown out as a yellow precipitate, which was purified by crystallization from alcohol or from glacial acetic acid.

The pure anil crystallizes in long yellowish needles, melting at 205.5° (corr.). It is soluble in alcohol, ethyl acetate, chloroform, or benzene, when hot; slightly soluble in hot water, or cold acetic acid; very difficultly soluble in acetone, ether, carbon disulphide, or naphtha.

Calculated for $C_{14}H_{10}O_2N_2$: N, 11.80. Found: N, 11.93.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
March, 1906.

THE OPTICAL ROTATION AND THE DENSITY OF ALCOHOLIC SOLUTIONS OF GLIADIN.

BY W. E. MATHEWSON.

Received February 12, 1906.

THE recent application of the polariscope to the estimation of gliadin[1] has rendered desirable some further knowledge regarding the specific rotation of this substance. With many substances optically active in solution, the specific rotatory power changes in a marked manner with changes in temperature, concentration, and nature of the solvent. The experiments given below were carried out by the writer with the view of determining the error that might be introduced into an analytical estimation by such variations.

The gliadin used had been prepared from a hard wheat patent flour by a method used by Osborne and Voorhees.[2] A small sample dried for twenty days in a vacuum over sulphuric acid

[1] H. Snyder: This Journal, 24, 263.

[2] Am. Ch. J. 15, 416, preparation No. 17.

gave 17.65 per cent. and 17.57 per cent. of nitrogen respectively by duplicate determinations made by the Kjeldahl-Dyer method. The standard hydrochloric acid used in these and other determinations had been standardized with silver nitrate in the usual way and checked against pure acetanilide. The proteid was soluble to a perfectly clear solution in dilute alcohol. It is extremely difficult to dry any considerable amount of gliadin within a reasonable length of time, the desiccation being carried out at ordinary temperatures over sulphuric acid *in vacuo*. Most of the material used was therefore merely dried for a few days in the vacuum desiccator and the concentration of the solutions made were found by determining the nitrogen in a given volume. Although the strength of the solution is not fixed as exactly in this way as by weighing out the pure substance, the error introduced is small and possible chemical changes produced in the proteid by removal of the last traces of moisture are avoided.

The polarimetric observations were made with a triple-shadow saccharimeter. In a few cases where the room temperature was considerably above 17.5° C. a small correction was introduced for the increase in the rotatory power of the quartz wedge compensation. Errors due to the difference between the rotation dispersion of quartz and of the solution would probably be much less than the error of experiment and would, of course, affect all observations of a series in a similar way. The temperature of the solution under observation was controlled in the usual way with a jacketed tube. The readings are the means of six observations.

Effect of Variation in Concentration of Gliadin.—The first point considered was the effect on the specific rotation of varying the gliadin concentration. A strong solution in 70 per cent. alcohol was prepared, the polarization determined, and duplicate portions taken for the nitrogen determination. Other amounts were measured off, and by successive dilutions with 70 per cent. alcohol, solutions of different concentrations obtained. The polarizations of these were determined. The following table shows the polariscopic readings (in Ventzke degrees) with solutions of different concentrations. In the third column are given the calculated readings, assuming the gliadin to have a specific rotation $[\alpha]_D^{20°} = -91.3$.

Gram of gliadin in 1 cc.	Observed reading	Calculated reading.
0.05390	—28.38° V.	(—28.38° V.)
0.03601	—18.97° V.	—18.96° V.
0.02406	—12.81° V.	—12.67° V.
0.01607	— 8.54° V.	— 8.46° V.
0.01074	— 5.75° V.	— 5.66° V.
0.007176	— 3.88° V.	— 3.78° V.
0.004795	— 2.60° V.	— 2.53° V.

Similar experiments with solutions in 75 per cent. alcohol gave the following:

Gram of gliadin in 1 cc.	Observed reading.	Calculated reading. $[\alpha]_D^{20°} = -89.2$.
0.01989	—10.12° V.	(—10.12° V.)
0.01329	— 6.70° V.	— 6.76° V.
0.00888	— 4.49° V.	— 4.52° V.

A solution in 80 per cent. alcohol containing 0.01625 gram per cubic centimeter (measured at 45° C.) gave a reading of —7.89° V. at 50° C. Diluted with an equal volume of 80 per cent. alcohol, the reading at 50° C. was —3.92° V.

These results indicate that the specific rotation is little affected by ordinary changes in the gliadin concentration. The apparent slight increase on dilution observed with the solution in 70 per cent. alcohol may have been due to loss of solvent by evaporation when the dilutions were made, although special care was taken to minimize this. As this loss results in an increase in the percentage of water in the remaining solvent, the chance of error is increased, as will be shown later.

Effect of Variation in Temperature.—A gliadin solution in 70 per cent. alcohol, containing 0.0539 gram per cubic centimeter at 20° C. gave the following readings at different temperatures:

Temperature.	Reading.	Specific rotation, $[\alpha]_D$
20°	—28.38° V.	—91.3
25°	—28.59° V.	—92.4
30°	—28.60° V.	—92.9
35°	—28.53° V.	—93.0
40°	—28.48° V.	—93.1
45°	—28.48° V.	—93.6

In calculating the specific rotations given above the change in length of the glass polariscope tube was so small that it was not taken into account. The expansion of the solution was deter-

mined and found to be approximately regular for this range of temperature, and equal to about 0.1 per cent. per degree. A solution in 75 per cent. alcohol gave the following:

Temperature.	Reading.
20°	—10.12° V.
25°	—10.17° V.
30°	—10.18° V.
35°	—10.10° V.
40°	—10.02° V.
45°	—10.07° V.

A solution in 80 per cent. alcohol of sufficient concentration to give a reading of —7.89° V. at 50° C. was cloudy from separation of gliadin at 45° C. It contained 0.01625 gram of gliadin per cubic centimeter, measured at 45° C. As the solubility of gliadin in strong alcohol increases so rapidly with rising temperature as to indicate a change in phase, solutions in 80 per cent. alcohol, remaining clear when cooled to 25° C., were too dilute to afford measurements of value.

Effect of Varying the Alcohol Concentration of the Solvent.—The preceding data show that with solutions in 70 per cent., 75 per cent. and 80 per cent. alcohol there is a marked increase in specific rotation with increase in percentage of water in the solvent. Below are the values obtained:

Concentration of alcohol in solvent. Per cent.	Specific rotation at 20° C. $[\alpha]_D^{20°}$.	Specific rotation at 45° C. $[\alpha]_D^{45°}$.	Specific rotation at 50° C. $[\alpha]_D^{50°}$.
70	91.3	93.6	....
75	88.2	90.0	....
80	....	....	84.6

As a check a sample of gliadin that had been drying for about ten days was taken and thoroughly mixed. Two portions were then weighed out and dissolved in 70 per cent. and 75 per cent. alcohol, respectively, and made up to known volumes. The apparent specific rotation of the first at 25° C. was —90.3°; that of the second at 40° C., —88.0°. Calculating from the first rotation, taking $[\alpha]_D^{25°}$ —92.4°, the sample contained 2.2 per cent. of moisture. Correcting the second for this we get for the solution in 75 per cent. alcohol $[\alpha]_D^{40°}$ —90.0°. An experiment in which a solution in 70 per cent. alcohol was diluted with sufficient water to bring the alcoholic concentration to about 66 per cent. indicated that a further change in the specific rotation was thus produced, the latter increasing with the increase of water concentration.

As Fleurent[1] has published a method for the approximate determination of gliadin in flours from the density of the alcoholic extract, made under prescribed conditions, it was thought desirable to determine the specific gravity of solutions containing the proteid in different concentrations. The following table shows the density of solutions of different concentrations in 70 per cent. alcohol. They were taken with a pycnometer.

Gram of gliadin per cc.	Specific gravity 20°/4°.
0.05390	0.8865
0.03601	0.8815
0.02406	0.8777
0.01607	0.8745
0.01074	0.8729
0.007176	0.8717
0.004795	0.8702
0.000000	0.8686

It would appear from this that even an approximate determination of gliadin in alcoholic solutions by means of the density would be quite difficult, as the change in specific gravity for a given change in the gliadin concentration is not especially large, and the disturbing effects of evaporation which would decrease the alcohol concentration of the solvent, absorption of moisture from the flour and variation in temperature could easily vitiate the results.

SUMMARY.

The specific rotation of gliadin in 70 per cent. to 75 per cent. alcohol is practically independent of the gliadin concentration.

With 70 per cent. to 80 per cent. alcohol it decreases with increase in the alcohol concentration.

Increase in temperature between the limits 20–45° C. produces a slight increase in the specific rotation.

The change in density in gliadin solutions for such differences as would be met with in flour analysis would allow rather a narrow margin for experimental error.

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[1] Abs. in J. Soc. Chem. Ind. **20**, 941, from Compt. rend. **132**, 1421.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 120.]

THE OSAZONE TEST FOR GLUCOSE AND FRUCTOSE AS INFLUENCED BY DILUTION AND BY THE PRESENCE OF OTHER SUGARS.

BY H. C. SHERMAN AND R. H. WILLIAMS.

Received February 26, 1906.

MAQUENNE[1] found that the reducing sugars when treated in a uniform way with phenylhydrazine showed considerable differences both in the yield of osazone and in the time required for the appearance of the osazone precipitate. Mulliken[2] has studied these differences in rapidity of osazone formation and makes use of them to an important extent in his scheme for the identification of pure sugars. According to Mulliken, 0.1 gram sugar, 0.2 gram pure phenylhydrazine hydrochloride, 0.3 gram sodium acetate and 2 cc. water are mixed in a small test-tube, corked loosely to prevent evaporation and heated in boiling water. If the tube is occasionally shaken without removing it from the boiling water, the osazone precipitate usually separates out quite suddenly so that duplicate experiments usually give results that agree within half a minute. Under these conditions the time required for the appearance of the osazone in the hot solution is given by Mulliken as follows: Fructose, two minutes; sorbinose, three and one-half minutes; glucose, four to five minutes; xylose, seven minutes; rhamnose, nine minutes; arabinose, ten minutes; galactose, fifteen to nineteen minutes. Sucrose, after about thirty minutes' heating, is sufficiently hydrolyzed to yield a precipitate of osazone. Maltose and lactose give no precipitate in the hot solution even when the heating is continued for two hours.

In our experiments we have followed closely the conditions adopted by Mulliken except that, for greater convenience of manipulation, twice the quantities were used throughout. Having confirmed the results above given for glucose, fructose, sucrose, maltose and lactose at the standard dilution, we determined the times required for the osazone precipitation with smaller amounts of glucose or fructose in pure solution and also when different

[1] Compt. rend. 112, 799.

[2] "Identification of Pure Organic Compounds."

amounts of other sugars were present at the same time. Every test was carried out as has been described, using 0.4 gram phenylhydrazine hydrochloride, 0.6 gram sodium acetate, and 4 cc. water, so that the only variable factor was the amount of sugar or sugars present. The tabular statements which follow show the time required for the appearance of an osazone precipitate in each case.

PURE SOLUTIONS OF GLUCOSE, FRUCTOSE, INVERT SUGAR, AND SUCROSE.

Weight of sugar taken. Gram.	Glucose. Minutes.	Fructose. Minutes.	Invert sugar. Minutes.	Sucrose. Minutes.
0.2	4–5	1¼–1½	1½–1⅔	31
0.1	5	1¾–2	2	35
0.05	6½	2½	3	78
0.01	17	5½	6–6½	No ppt.
0.005	34	10	14	
0.0025	65	17		

With less than 0.005 gram glucose or 0.0025 gram fructose, the amount of osazone separating in the hot solution was small and the time of its appearance doubtful.

INFLUENCE OF MALTOSE ON GLUCOSE.

Weight of glucose. Gram.	Weight of maltose.				In absence of maltose.
	0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	
0.01	No ppt.	40 min.	30 min.	22 min.	17 min.
0.02	26–28 min.				12–13 min.

INFLUENCE OF LACTOSE ON GLUCOSE.

Weight of glucose. Gram.	Weight of lactose.				In absence of lactose.
	0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	
0.01	No ppt.	50 min.	32 min.	25 min.	17 min.
0.02	45–48 min.				12–13 min.

It is evident that both maltose and lactose interfere seriously with the formation and precipitation of glucosazone and that the influence of lactose is greater than that of maltose. Thus a mixture of 0.01 gram glucose and 0.1 gram lactose required ten minutes' longer heating than a parallel mixture with 0.1 gram maltose, and when the quantities of glucose, lactose, and maltose are doubled (the amounts of reagents and the volume of the solution remaining the same) the lactose mixture required twenty minutes' longer heating than the maltose mixture.

INFLUENCE OF SUCROSE ON GLUCOSE.

Weight of glucose. Gram.	Weight of sucrose. 0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	In absence of sucrose.
0.005	15–17 min.	15–17 min.	22 min.	30 min.	33–39 min.
0.01	14–16 min.	16 min.	17 min.	17 min.	17 min.
0.2	9 min.				12–13 min

INFLUENCE OF RAFFINOSE ON GLUCOSE.

Weight of glucose. Gram.	Weight of raffinose. 0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	In absence of raffinose.
0.005	27–30 min.	33–37 min.	36–38 min.	37–39 min.	33–39 min.

INFLUENCE OF MALTOSE ON FRUCTOSE.

Weight of fructose. Gram.	Weight of maltose. 0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	In absence of maltose.
0.01	7–8 min.	5½–6 min.	5½–5¾ min.	5½ min.	5½ min.

INFLUENCE OF LACTOSE ON FRUCTOSE.

Weight of fructose. Gram.	Weight of lactose. 0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	In absence of lactose.
0.01	9½–10 min.	7¾ min.	6¾ min.	6 min.	5½ min.

Comparing these results with the corresponding figures for glucose it will be seen that the interference of maltose and lactose is less marked with fructose than with glucose. In both cases, however, the appearance of the osazone precipitate is retarded distinctly by maltose and to a greater extent by lactose.

INFLUENCE OF SUCROSE ON FRUCTOSE.

Weight of fructose. Gram.	Weight of sucrose. 0.2 gram.	0.1 gram.	0.05 gram.	0.01 gram.	In absence of sucrose.
0.005	8½ min.	8¾ min.	9⅓ min.	9¼ min.	9½ min.

SUMMARY OF RESULTS.

In pure glucose solutions tested at constant volume with fixed amounts of phenylhydrazine hydrochloride and sodium acetate the time required for the precipitation of osazone varies with the amount of glucose present and is nearly constant for any given dilution.

Pure solutions of fructose show similar variations with concentration but always yield a precipitate of osazone in about one-third the time required by the same amount of glucose.

From invert sugar solutions the osazone precipitates almost as rapidly as from fructose solutions of the same concentration.

In solutions containing only about 0.1 per cent. of glucose the time required for the precipitation of osazone is shortened con-

siderably by the presence of 1 per cent. or more of sucrose; only slightly by the presence of 5 per cent. of raffinose.

Sucrose also accelerates the osazone precipitation in dilute solutions of fructose, but as these react much more rapidly than the corresponding glucose solutions, the effect of the sucrose is scarcely noticeable.

Maltose retards the precipitation of glucosazone, interfering much more seriously in the case of glucose than in the case of fructose.

Lactose interferes with the glucosazone test in a similar manner and to a greater degree than maltose.

The bearing of these results upon the analytical application of the osazone reaction is too evident to require detailed discussion.

We plan to continue this work by studying the influence of maltose, lactose, and sucrose upon the yield and physical properties of glucosazone and later to extend the investigation to other substances and to the corresponding reaction with derivatives of phenylhydrazine.

QUANTITATIVE LABORATORY,
February 6, 1906.

THE SAMPLING OF COAL AND CLASSIFICATION OF ANALYTICAL DATA.

BY A. BEMENT.

Received December 20, 1905.

IF A history of the sample of coal were given with the results of the analysis, it would be of great service, and if this becomes standard practice, one would be able to arrive at a more definite conclusion as to what an analysis represented. It is very often the case that the chemist analyzes a sample stated to be representative of a certain mine, seam, locality or kind of coal, and yet knows nothing regarding its selection; the result is, that he may present a report that is erroneous, because the sample may have been a picked one, better than is possible with the average product. Or, on the other hand, it may be an inferior one, with the result that in each case the chemist's work does not appear to the best advantage. A comparison of various published analyses of what is presumably the same coal, will show a most confusing series of results that cannot be explained by any assumption that the analytical methods differ. Many of the composi-

tions given, particularly in engineering text-books, are from analyses of coal used in boiler trials, and as it is quite often the case that selected fuel is used, it results in a value unduly high being assigned to the coal by those who do not know the source of the sample.

Often samples are taken from a seam in mines, and presented as representing the coal shipped to the consumer, when the more exact method would be to sample the product loaded for shipment. Or again, a seam may be sampled without it being stated whether the object was to determine its entire composition, or that portion supposed to be taken for shipment. It is the author's opinion that the sampling is as important as the analysis, and that the person receiving results of analysis should insist on a statement giving the history and description of the sample, and that the chemist would advance his interests by insisting on a full statement when practicable. At all events, if those who receive reports of analyses would use discretion in accepting results in the absence of such history and description of the sample, it would tend to the avoidance of confusion, and compel better practice.

Not only the interests of the consumer and purchaser demands better sampling methods, but the matter is of even greater importance to the dealer or producer. Assuming the heating power of semi-bituminous coal at 14,000 B. T. U. as a maximum value for coal, and screenings or "slack" at 9,000 B. T. U. as a minimum value, and that an unscrupulous dealer should substitute the latter for the former fuel, the purchaser would be the loser by 36 per cent. This would represent the maximum opportunity for the dealer to defraud the purchaser, because the coal producer would not cause the miners to add dirt to the fuel for the purpose of increasing the quantity, for the reason that he would have to pay more for mining rock and clay than for coal. Thus the producer, dealing with large quantities, cannot afford to purposely adulterate his goods. The unscrupulous purchaser, on the other hand, in the preparation of a sample—a very small quantity—is not limited by reason of cost in the quantity of foreign matter taken, even to the total exclusion of combustible, but assuming a composition of 90 per cent. foreign matter, the seller may be the loser by 89 per cent. Thus by carrying these considerations to their maximum ranges, there appears the possibility of greater variation in the quality of the sample, than in the fuel supply.

The sampling is fully as important, should be conducted under as reliable auspices, and safeguarded as much as the analysis.

DETERMINATION OF VOLATILE MATTER.

The author considers it most desirable and necessary that a more reliable method of volatilization be adopted. The chemist finds volatile matter in coke which has been some days at a considerable temperature in an oven. From this it may be concluded than an important interval of time and a high temperature are essential to the operation, but with present practice, if heating is continued beyond a certain unknown interval, the combustion of fixed carbon becomes greater in amount than that of the unexpelled volatile matter. For this reason it appears necessary to effect volatilization in an inert atmosphere that distillation may be more effective and without combustion of fixed carbon. The most that has been expected from the best established method is that it gives "concordant" results. It is the author's conviction, however, that such results are neither concordant nor correct, and he is now disposed to advocate the use of hydrogen as an inert atmosphere rather than nitrogen, because of its greater simplicity of production and purification.

FORMS OF ANALYSIS AND RELATIVE COMPOSITION.

The engineer requires the relative composition of the moist and dry coal, and what is often erroneously called the combustible, to be stated, while it is more often the practice of the chemist to present only the constituents and values of the moist coal. For reasons given later, it will appear that the engineer's requirements are justified, therefore such demands are recognized and considered in the following treatment.

From the standpoint of the proximate analysis, it is useful to consider coal in four divisions, and the relation is illustrated by the following three equations:

1. $\left.\begin{matrix}\text{Fixed carbon}\\ \text{Hydrocarbons}\\ \text{Sulphur}\end{matrix}\right\} + \left\{\begin{matrix}\text{Water of composition}\\ \text{Nitrogen}\end{matrix}\right\} = \left\{\begin{matrix}\text{Pure coal.}\end{matrix}\right.$
2. Pure coal + ash = Dry coal.
3. Dry coal + moisture = Moist coal.

The combination designated "water of composition" is proposed by Parr.[1] Following this scheme the author has adopted the arrangement presented in Tables I and II, wherein the moist,

[1] This Journal, 26, 294; Bull. Univ. of Ill., July 15, 1904.

dry, pure coal and combustible compositions are given. As shown, three divisions or analyses are presented, namely, usual proximate, what the author designates as an extended proximate, and an ultimate analysis of the pure coal, the elements being also presented in the other columns at their respective values. The author is indebted to C. H. McClure for the classification in the three latter divisions. It is not the author's intention to propose methods for analysis, but to offer a system of classification which will display relative values of different coal compositions, as shown in Tables I and II, and while these tables are sufficient in themselves to illustrate the proposition, it is well to present the source of the data used in compiling them, which represents two coal seams in Illinois.

The analytical work consisted of the usual proximate analysis, and the determination of total carbon according to Parr. Sulphur and nitrogen were separately obtained. Available hydrogen is calculated by $\frac{Total\ Carbon—Fixed\ Carbon}{5}$, the value for fixed carbon being obtained by the usual proximate analysis. This hydrogen ratio was proposed for Illinois coals by Parr, and is considered to be a constant, and its determination required analyses wherein carbon and hydrogen were obtained by combustion, but it may also be determined by $H—\frac{O}{8}$.[1] It is not the author's object to propose the acceptance of Parr's method of determining available hydrogen, but to insist upon recognition and presentation of the inert matter in the pure coal, for which there is as much reason as with that other inert matter, namely, the ash. In fact, as the determination of available hydrogen is dependent on his ratio, which is of itself dependent on an ultimate analysis, and as it is considered as a constant, it might be best to establish such factors directly by ultimate analysis.

Thus the source of the data for the compositions in the three divisions of Tables I and II is as follows:

Total carbon, method of Parr.

Fixed carbon, by usual proximate analysis.

Available hydrogen, calculated according to hydrogen ratio.

Water of composition, by difference.

[1] In some cases, at least, this formula does not give correct values for available hydrogen.—EDITOR.

Sulphur and nitrogen, by separate determinations.
Ash and moisture, by proximate analysis.
Heating power, by calorimeter.

The presentation of values in the four columns shows how and wherein the two seams differ, and illustrates their true relation. For example, the fixed carbon in the moist coal of Table I appears higher than in that of Table II, but an inspection of the pure coal columns which give the true relative values, shows that it is just the reverse, because the ash and moisture of the moist coal differ in amount; thus a proper comparison between the two coals cannot be made unless the values are presented on a common basis. Likewise, the values for available hydrogen show why the heating power of the combustible of No. I is higher than with No. II, and an explanation of the difference in heating power of the moist and dry coal is principally afforded by the ash and moisture of these compositions. Following the consideration of relative composition further, Table III is presented, wherein the essential features of the two coals are shown in parallel columns, from which the relation can be directly noted.

Inasmuch as Parr proposes a constant, that of the hydrogen ratio, the possibility of the more extended use of constants is presented, and the author urges the feasibility of considering the pure coal compositions as constants for a coal seam, or particular locality of such seam. This possibility has been suggested, principally by the fact that the heating power of the pure coal from a general locality does not vary over greater limits than that of the calorimetric method, and he has been able to employ it as a constant in calculating the heating power of dry and moist coal, having determined only moisture and ash, and obtained results that check with calorimetric determinations made on the same samples. The author, however, does not claim originality in this observation, but does insist that the use of such constants is of advantage.[1]

[1] A better method of calculating the pure coal would seem to be that suggested by the Committee on Coal Analysis, in this Journal, 21, 1131, where it is recommended "that the combustible matter of the coal be calculated by subtracting from 100 the per cents. of ash and moisture and one-half of the sulphur." This recommendation was based on the fact that the sulphur in coal is usually largely in the form of pyrites, and when in this form it is replaced in the ash by three-eighths of its weight of oxygen. If

It is a fact that coal from a general locality has been analyzed over and over again, with always a more or less different result when presented in only the moist coal composition, so that after all of the multiplicity of work, a final conclusion or full understanding is still unattained. It appears to the author, that instead of so much superficial work, it would be better that a limited amount of more thorough investigation be made, with the object of determining values of the combustible, and particularly the pure coal. There would then be more opportunity to consider the two great variables, namely, ash and moisture, and a number of such values could be collected, thus establishing standards. This would also be of great assistance in coal inspection service, because locality and coal seam being known, it would be essential to determine only ash and moisture, and specifications governing these constituents only need be drawn.

This view concedes that coal from a certain locality or seam does not vary in quality, but that the variation is due to the presence of ash and moisture, which are impurities associated with coal.

As illustrating the matter of treating the constituents and values of the pure coal as constants, the composition in Tables I and II are made up from values taken from different sources. Ash, moisture and heating power are the average of a number of samples taken from the full height of the two seams, and the determinations were made under the author's direction. Nitrogen was determined on the author's samples by another chemist. All other values are from work done by S. W. Parr on different samples from the same seams.

THE TERM PURE COAL.

The word combustible, used more particularly by engineers to designate fuel free from ash and moisture, is erroneous and confusing, therefore the author has adopted the term pure coal; the expression "coal free from ash and moisture" is more definite

the combustible matter, or "pure coal," of the coal is calculated by this formula, it will be found that for a given seam of coal the heat of combustion of the combustible matter is very nearly constant. Thus for Coal 1 in the analysis given below the heat of combustion of the combustible matter is 14,747 B. T. U., while that for No. 2 is 14,457 B. T. U., and it would probably be found that the heat of combustion of the combustible matter of other samples of coal from these respective seams would agree very closely with these values.—EDITOR.

and self-explanatory, but it is composed of many words and is cumbersome. Objection has been made because it contains sulphur, which was regarded an impurity, but all coals contain it, and as the volatile portion must be considered as in chemical combination, it is necessarily always a constituent, and cannot be separated without destroying the combination. Thus the term pure coal is justifiable, and the ultimate conception of coal is this pure coal, having associated with it, but not in combination, the two impurities, moisture and ash, the fixed sulphur being considered one of the constituents of the ash.

TABLE I.

	Moist coal.	Dry coal.	Pure coal.	Combustible.
1. Usual proximate analysis:				
Moisture	6.29	....	....	....
Ash	8.74	9.33	....	....
Volatile matter	34.91	37.25	41.08	....
Fixed carbon	50.06	58.92	58.92	....
2. Extended proximate analysis:				
Moisture	6.29	....	....	....
Ash	8.74	9.33	....	....
Carbon, total	68.06	72.63	80.11	93.90
Carbon, fixed	50.06	53.42	58.92	69.06
Volatile combustible	22.41	23.92	26.38	30.94
Water of composition	11.09	11.82	13.04	....
Hydrogen (available)	3.60	3.84	4.24	4.97
Sulphur, volatile	0.82	0.87	0.96	1.13
Sulphur, fixed	0.76	0.82	....	....
Sulphur, total	1.58	1.69	0.96	1.13
Nitrogen	1.41	1.51	1.66	....
Total non-combustible	27.53	22.66	14.70	....
Total combustible	72.47	77.34	85.30	100.00
B. T. U. per pound	12,416	13,250	14,613	17,131
3. Ultimate analysis:				
Carbon	68.06	72.63	80.11	93.90
Hydrogen	4.99	5.32	5.87	4.97
Oxygen	9.70	10.34	12.41	....
Nitrogen	1.41	1.51	1.66	....
Sulphur	1.58	1.69	0.96	1.13

TABLE II.

	Moist coal.	Dry coal.	Pure coal.	Combustible.
1. Usual proximate analysis:				
Moisture	9.91	....	....	....
Ash	11.51	12.78	....	....
Volatile matter	30.16	33.47	38.38	....
Fixed carbon	48.42	53.75	61.62	....

TABLE II (*Continued*).

	Moist coal.	Dry coal.	Pure coal.	Combustible.
2. Extended proximate analysis:				
Moisture	9.91	....	....	....
Ash	11.51	12.78	....	....
Carbon, total	63.55	70.54	80.87	94.73
Carbon, fixed	48.42	53.75	61.62	72.20
Volatile combustible	18.65	20.70	23.73	27.80
Water of composition	10.28	11.40	13.08	....
Hydrogen (available)	3.03	3.36	3.85	4.51
Sulphur, volatile	0.50	0.57	0.65	0.76
Sulphur, fixed	0.70	0.78	....	....
Sulphur, total	1.20	1.35	0.65	0.76
Nitrogen	1.23	1.37	1.57	...
Total non-combustible	32.93	25.55	14.65	....
Total combustible	67.07	74.45	85.35	100.00
B. T. U. per pound	11,348	12,596	14,442	16,921
3. Ultimate analysis:				
Carbon	63.55	70.54	80.87	94.73
Hydrogen	4.31	4.78	5.48	4.51
Oxygen	9.00	9.97	11.43	....
Nitrogen	1.23	1.37	1.57	....
Sulphur	1.20	1.35	0.65	0.76

TABLE III.—RELATIVE CONSTITUENTS OF COALS NOS. 1 AND 2.

	Coals.	
	No. 1.	No. 2.
Combustible:		
Carbon, total	93.90	94.73
Carbon, fixed	69.06	72.20
Volatile combustible	30.94	27.80
Hydrogen (available)	4.97	4.51
Sulphur, volatile	1.13	0.76
B. T. U.	17,131	16,921
Pure coal:		
Water of composition	13.04	13.08
Nitrogen	1.66	1.57
Total non-combustible	14.70	14.65
B. T. U.	14,613	14,442
Dry coal:		
Ash	9.33	12.78
Fixed sulphur	0.82	0.78
B. T. U.	13,250	12,596
Moist coal:		
Moisture	6.29	9.91
B. T. U.	12,416	11,348

215 DEARBORN ST., CHICAGO, ILL.

SOME NOTES ON THE SERVICE WATERS OF A RAILWAY SYSTEM.[1]

By S. W. Parr.

Received March 10, 1906.

All of our railway systems that traverse considerable portions of the country meet with very numerous and often interesting varieties of water which must be made use of in locomotive service.

It is unnecessary to detail here the disadvantages of a poor water. Opportunity was afforded recently to verify some of the statements often quoted concerning the loss of heat due to the presence of scale of a given thickness. A test of steaming efficiency was made at the University of Illinois,[2] on a locomotive having a thickness of scale averaging one-eighth of an inch. After overhauling and cleaning, a second test was made which showed a heat loss of 10.5 per cent. due to the one-eighth of an inch scale.

This agrees closely with a comparison made some time previously on the same road. The performance sheets of one hundred and twenty locomotives were taken with reference to the consumption of coal for three months next preceding an overhauling and cleaning, and these results were compared with the coal consumption for the three months immediately following such a cleaning, with an average showing for the one hundred and twenty engines, of almost exactly 10 per cent. in favor of the scale-free condition.

The annual fuel bill on one of the roads of the Middle West is approximately $1,500,000. Suppose half the locomotives on the system to be clean and working at their proper efficiency, and the other half possessed of the above average thickness of scale; 5 per cent. additional cost for fuel would represent an annual tax of $75,000, due to this cause alone.

Duplicate this expense with another which would represent approximately the cost of overhauling and repairs, chargeable directly to the presence of scale, and we have a sum representing the annual interest at 5 per cent. on an investment of $3,000,000. This takes no account of interest on the large number of con-

[1] Read at the New Orleans meeting of the American Chemical Society.

[2] R. R. Gazette, June 27, 1899.

tinuously idle engines under repair, nor of the cost of accidents or disasters due more or less directly to bad waters.

Throughout the Middle West, at least, an interesting transformation is going on in connection with the attitude of railways, in that at least five of the most extensive systems have equipped, or are in process of installing purification plants for the treatment of their service waters. This is in marked contrast to the condition existing ten years ago, when in the same region not a single plant existed for the treatment of the water to be furnished locomotives.

It should not be inferred from this fact that no interest was taken in the matter by the railways at that time. Indeed, that might well be termed the "era of soda-ash," for most of the roads were then using that or similar material in the tender tanks of their locomotives. Other substances were also used, such as trisodium phosphate, petroleum mixtures, etc., and a rather thorough trial was given to various schemes of interior treatment within the locomotive boiler, with the general result that such methods were abandoned as unsatisfactory.

Concerning interior treatment, it may be noted that in very many instances, in the case of stationary boilers, the conditions are entirely favorable for making use of the interior of the boiler for effecting a purification of the water. By analogy it would seem that a locomotive boiler could be made to serve a similar purpose, but such is not the case. Here the sum total of interior space is so small in proportion to the steaming capacity of the boiler that a very definite limit is set to the density or viscosity of the residual water. It seems pretty thoroughly demonstrated that the limitations of space and the element of time, as well as the character of the chemicals which must be used, make interior treatment, in the case of locomotive boilers, as a general proposition, inadvisable. The resulting practice, therefore, seems inevitable, *viz.*, that of previous purification, so that the water as served to locomotives must be in the best possible condition.

As illustrating the wide variation in waters, as well as certain interesting types, the following examples are selected: A considerable number of waters have come to hand with but from 2 to 3 grains of incrusting solids, and a content of total solids not exceeding 6 or 8 grains per gallon. These waters, some twenty-five in number, are from the Illinois Central Railway Company,

mainly in Mississippi and Louisiana, though some come from Kentucky, and one from Cairo, Illinois.

At first thought, it might be concluded that these are surface waters or waters from shallow wells in the Mississippi Delta, where the soil formation is such as to yield but little to the solvent action of the water. This, however, is only partially true. A well at Covington, Tenn., with a depth of 538 feet, shows incrusting matter to the amount of only 4.05 grains per gallon, and total solids of 5.56 grains per gallon. A well at Cairo, Illinois, 400 feet deep, shows only 5.9 grains of scaling matter, and only 8.6 grains of total solids. A number of wells from 100 to 200 feet in depth show less than 5 grains of scaling matter, and less than 8 grains of total solids, while perhaps most remarkable of all is a well at Hammond, Louisiana, 2100 feet in depth, showing scaling matter to the extent of only 5.5 grains, with free sodium carbonate amounting to 5.9 grains, the total solids being only 12 grains per gallon. Another water of this region with a depth of 825 feet has almost the same composition, *viz.*, scaling matter 3.9 grains, free alkali 4.5 grains, and total solids less than 10 grains.

It is evident under these conditions, that there is little, if any, scale formation in the boilers, and we have, therefore, an altogether different problem to deal with, namely, that of corrosion. Corroding conditions no doubt exist in many waters which produce scale, but the protection afforded by the scale prevents that action which would normally occur if the same water were continually in contact with the clean iron. The statement is occasionally met with that iron immersed in pure water may remain indefinitely without rusting. The statement is also sometimes made that the purer the water the more corrosive its action. In studying the conditions which promote the corrosion of iron, the following experiments were conducted:

In an autoclave which could be maintained under a steam pressure of one hundred pounds, there was placed a beaker of distilled water with a weighed quantity of fine wire in short pieces (card teeth). Heat and pressure were maintained for two hours with the result that there was evident corrosion. This experiment was repeated a number of times for verification. Next, the test was repeated, but the conditions were varied by first thoroughly boiling the distilled water. The amount of corrosion was greatly reduced.

A third series of tests was made wherein the iron was added to the thoroughly boiled pure water, which had been placed in the open autoclave in which other water was vigorously boiling, so as to displace as far as possible the volume of air which would otherwise fill the spaces. The iron was then added and the autoclave sealed. Under these conditions the corrosion was practically eliminated.

This suggested another series of tests in which the same conditions as the last were maintained, but with the addition of a flask in which were pieces of marble and dilute sulphuric acid,—an arrangement which would slowly and for a considerable length of time evolve carbon dioxide, but with no chance of the acid solution coming in contact with the iron, this liberation of carbon dioxide being attended, of course, by conditions of temperature and pressure of one hundred pounds per square inch, as before. Here the corrosion of the wire was very marked, much exceeding that of any of the previously outlined experiments.

Still another series of tests was suggested from these results. The same conditions were observed as in the last case, except that, instead of the flask with its marble and acid, there was substituted a shallow dish with sodium peroxide. Here, as the steaming continued, oxygen would be liberated under the conditions of temperature and pressure as before. The extent of corrosion was again very marked, being equal in amount to that produced in the presence of carbon dioxide.

Further tests were made wherein the pure water was replaced by solutions with known amounts of magnesium or calcium chloride, or nitrate and sulphate of magnesium and of iron, as also very small amounts of tannic acid, in separate tests. As might be expected, all of these solutions, with the exception of the magnesium sulphate, were strongly corroding.

In repeating all these tests, with the addition of sufficient sodium carbonate to produce slight alkalinity to the water submerging the iron, the corrosion was stopped, or at least reduced to an indeterminate amount in the time allotted for the tests.

Returning now to the non-scaling type of these southern waters under discussion, two conditions are to be noted: (*a*) Those waters from bayous, creeks and shallow wells hold in solution much organic matter; (*b*) those waters from greater depths, say 100 feet and more, contain, as a rule, from 2 to 6 grains per

gallon of free sodium carbonate. Out of twenty-one waters, seven are thus provided with free sodium carbonate and seventeen are without, yet having high organic matter. Now in actual experience, in the region where these waters occur, there is some trouble from corrosion. The conclusions as to the cause are obvious. Where organic matter abounds the resulting organic acids in themselves are corroding. Where such waters mix with others having free sodium carbonate, the corroding conditions are accentuated up to the point where the sodium carbonate water is used in excess. You will see from this that there is no place given for the theory held by some, that sodium carbonate produces corrosion in boilers. It is true that a casual or perhaps superficial view of the waters above described would lead to the conclusion that the corrosion is due to the sodium carbonate naturally present in the waters, but I have yet to meet with a thoroughly authenticated case of corrosion due to the presence of free alkali in reasonably moderate amounts.

This matter of free alkali assumes a far greater importance than formerly. This brings me to a discussion of a type of water now very commonly met with farther north, more especially as far as my own experience goes, in Illinois. These waters are seldom met with at a less depth than 100 or 125 feet. They are characterized by the presence of free sodium carbonate and the absence of sulphates, at least no more than sufficient to satisfy a portion of the alkalies present. The free sodium carbonate ranges from 3 or 4 grains to 15 or 20 grains per gallon. The scaling ingredients are of course in the form of bicarbonates, and often present in amounts sufficient to place them by the ordinary classification as poor waters, or at least only fair, when, as a matter of fact, they are non-scaling and of superior quality.

At least one large area in Illinois has been developed where this water is found at a depth varying from 125 to 165 feet. With the University of Illinois as a center, it extends east and west approximately a total distance of 100 miles, and north and south about 40 miles. At other scattered points, the same type is met with at varying depths. At Burnside, near Chicago, this same free alkali type occurs again at a depth of 400 feet. At Wenona, 100 miles southwest, it occurs at a depth of 800 feet, but with an additional constitutent of sodium chloride amounting to 80 grains per gallon. At Carbondale again, 300 miles south of

Chicago, the same type is met with, having 15 grains of free sodium carbonate, no sulphate of lime, and 120 grains of salt per gallon. The depth is 850 feet.

It is readily seen that in use, with this type, the water in the boiler becomes more and more impregnated with free alkali. This very soon becomes a most active precipitating reagent for the fresh incoming water, the result being that no scale but only sludge forms inside the boiler. Outside of the boiler, in the feed water, *e. g.*, this condition does not exist; indeed the bicarbonate of lime present is in the best possible form for producing scale where only heat is applied, hence such waters scale badly in feed pipes as they approach the hot part of the boiler, as also in feed-water heaters and especially in heaters such as water-backs for household service.

One problem, and that often a serious one, presents itself in connection with this type of water, and that is the tendency to foam. A rather extensive series of tests, made in connection with a locomotive in heavy freight service on the Illinois Central, established the limit for alkaline salts of the sulphate and chloride sort as approximately 50 grains per gallon; that is, when an ordinary engine tank filled with such water has been all discharged into the boiler, the resulting concentration, bringing the ratio up to three or four times the initial amount of alkali, affords a condition to promote foaming when extra stress of work, such as a grade or greater speed, is imposed upon the engine. This tendency to foam is much enhanced by the presence of free alkali.

Now at first thought it might be concluded that the free alkali is the cause, but there is a strong probability that this is incidental and results from attending circumstances; for example, there are some evidences to show that foaming results directly from the presence of finely divided particles in suspension, and if this condition could be entirely eliminated, the presence of alkali in whatever form would be without effect so far as foaming is concerned. Turbid waters, and waters with very finely divided matter in suspension, approaching perhaps the colloidal condition, are especially susceptible to the presence of free alkali, in their tendency to foam. This is illustrated in the use of Mississippi river water in Illinois Central Railway locomotives which have previously received waters of the free alkali type from water

stations north of New Orleans, even though such waters have what would ordinarily be considered a low content of alkali. Foaming is a common difficulty after reaching the region where the intake is from the river.

The question as to what condition actually causes foaming is of great importance. Whether finely divided particles in suspension are responsible, may not now be an element in the case, for it may be argued that boilers are never free from this condition, but it is entirely conceivable that the waters of a division might receive such efficient treatment, both chemical and mechanical, as to eliminate all of the suspended matter.

The problems connected with railway service are altogether different, therefore, from those that attend the use of stationary boilers. They involve no very profound chemical principles, and perhaps on that account have received little attention; but the industrial importance of the matter is very great, and, if for no other reason, it may perhaps be worth mentioning as an illustration of an improved and more healthy state of affairs in the industrial world, which shows itself in giving attention to wastes and greater care in small economies. When we acquire, as there are many indications that we are attempting, the habit of looking after all possible wastes and losses, from principle, the profits are more sure to look out for themselves.

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A RAPID METHOD OF BABBITT METAL ANALYSIS.[1]

BY H. YOCKEY.

Received February 23, 1906.

THE following method of Babbitt metal analysis has been in use in this laboratory for eight or nine months, and has proved to be very satisfactory. While the principles and reactions involved are all old and well established, I have never been able to find them in print, put together in this manner and used for this purpose. The complete analysis requires from three to three and one-half hours.

Babbitt and bearing metals usually contain lead, antimony, tin and copper. Small amounts of zinc and arsenic are some-

[1] Read at the March meeting of the Cincinnati Section of the American Chemical Society.

times found, but these are usually volatilized during the heating the metals receive before casting.

Weigh and treat, in a small beaker or casserole, 1 gram Babbitt metal filings or borings with 20 cc. of nitric acid (sp. gr. 1.42) and water (1:2). Place on the water-bath and cover with a watch-glass. When spattering ceases, wash spatterings from the glass back into the beaker, and evaporate to dryness. Then bake in an air-bath one hour at 120°. Attention is called to the baking of the oxides, as without baking results are low. Moisten well with concentrated nitric acid and add 30–40 cc. hot water and boil vigorously five minutes. Filter off the mixed oxides of tin and antimony, wash with hot water, dry and ignite in a porcelain crucible, using a few drops of concentrated nitric acid to oxidize any metal reduced in burning the filter. Weigh as $Sb_2O_4 + SnO_2$.[1]

Dilute the filtrate from the above to 250 cc. in a calibrated flask. Take out with a pipette 50 cc. Add 10 cc. of ammonia (1 part of ammonia, sp. gr. 0.9, to one part of water) and 6 cc. glacial acetic acid. Heat to incipient boiling and titrate the lead with a solution of ammonium molybdate (1 cc. = 0.01 gram lead) which has been standardized against pure lead dissolved in nitric acid. Use tannic acid (1 to 300) as indicator.

To the remaining 200 cc. of the solution add sodium carbonate until a precipitate forms, then add 1 or 2 cc. of ammonia. Stir well, and allow to settle; if copper is present, the well-known deep blue color of the copper-ammonium ion will be observed. Then titrate with standard solution of potassium cyanide until the color disappears. The lead carbonate and hydroxide present do not interfere.

While conducting the above, weigh out a fresh portion[2] of Babbitt metal, and determine the antimony by the method by Andrews as described by Walters and Apfelder.[3] One gram of filings is treated in a 150 cc. beaker with 1 gram potassium iodide, 40 cc. concentrated hydrochloric acid (sp. gr. 1.2) and 40 cc. of water. Boil gently one hour, and filter, washing the precipitate

[1] This precipitate may contain some copper, iron and phosphorus.—ED.

[2] This Journal, 17, 872. [Andrews advises that the antimony be heated with sulphur and determined as sulphide.—ED.]

[3] Ibid. 25, 635.

with hot dilute hydrochloric acid (1:10), then with hot water, finally once with alcohol. Treat a duplicate filter-paper in the same way, dry both at 100° C. one hour and weigh the precipitate as metallic antimony. Calculate antimony to Sb_2O_4, and subtract the same from the weight of mixed oxides of tin and antimony, giving the weight of SnO_2 from which tin is calculated.

Copper is usually present in Babbitt and bearing alloys in small amounts, seldom over 1 per cent., and a weak solution of potassium cyanide is used for titrating. One cc. KCN = 0.0025 gram copper.

Results obtained by this method:

SAMPLE No. 1.

	1. Per cent.	2. Per cent.	3. Per cent.
Lead	78.47	78.60	78.54
Tin	12.09	12.06	12.06
Antimony	9.06	9.01	9.02
Copper	0.25	0.27	0.25
	99.87	99.94	99.87

Lead by $PbSO_4$ method = 78.55 per cent.

SAMPLE No. 2.

	1. Per cent.	2. Per cent.	3. Per cent.
Lead	68.76	68.86	68.84
Tin	15.93	15.83	15.79
Antimony	15.02	15.10	15.04
Copper	0.14	0.14	0.14
	99.85	99.93	99.81

Lead by $PbSO_4$ method = 68.82 per cent.

NATIONAL LEAD COMPANY, CINCINNATI, OHIO.

A STUDY OF CERTAIN METHODS FOR DETERMINING TOTAL SOLUBLE BITUMEN IN PAVING MATERIAL.

BY S. AVERY AND R. CORR.

Received January 2, 1906.

THE present paper presents the results of a comparative study of some of the numerous methods proposed for the determination of bitumen, soluble in carbon bisulphide, in the finished surface of an asphalt pavement.

The difficulties encountered in an exact determination have been well set forth by Dow.[1] The first thing to be considered is expressed in his note: "It has been claimed by some that mineral matter (which passes through the filter) is all in chemical combination with bitumen." In order to test this claim (a claim that Dow and other authorities do not endorse) a solution of Bermudez asphalt cement was forced through a Pasteur filter. The filtrate was evaporated in a platinum dish and ignited. The mineral matter left on ignition amounted to 0.06 per cent. of the bitumen taken. This amounts to about 0.006 per cent. of the total paving material as placed in the street, which, as will readily be seen, is an entirely negligible quantity. The following tables give the result of the comparison of the methods used.

The modified Soxhlet method used by the authors was conducted as follows: A piece of hardened filter-paper made by C. S. & S., Düren, No. 575, 11 cm. in diameter, was placed in the center of a cloth having about twice the diameter. The filter-paper and cloth were wet with distilled water and gradually pressed over the end of a test-tube about one inch in diameter, the cloth being outside. The two were held in place by rubber bands and the whole dried at a temperature of 110°. In this way a capsule of hardened filter-paper was prepared. This paper was extracted with carbon bisulphide, dried for one-half hour at 110°, cooled in a weighing-bottle and weighed. A weighed amount of the sample was placed in the filter-paper and the whole inserted into a Soxhlet extractor and extracted until the solvent had siphoned over perfectly colorless for some ten times. The solvent with the extracted bitumen was then ignited in a platinum dish and the percentage of residue determined. The filter-paper and its contents were then dried at 110°, cooled in a weighing-bottle and weighed. The loss in weight less the material recovered from the solvent represented the amount of dissolved bitumen.

The method of Dow is essentially a subsidence method, the details of which are given in the paper previously referred to. The supernatant liquid is finally filtered through a Gooch asbestos filter.

The method used in obtaining the figures in the table headed

[1] Proceedings for the American Society for Testing Materials, Vol. 3, 1905.

"Filtration and Washing on Asbestos Filter" is the method given by Richardson[1] for refined asphalt. It is not recommended by this author for determining the bitumen in the finished paving surface.

In preparing the following tables an attempt was made to show how closely duplicates could be secured, by the various methods, with material supposed to contain 10 per cent. bitumen and which had passed through 1.5 mm. sieve. The first three samples were Malthas and the remainder Bermudez. An attempt is also made to show the relative amounts of fine material recovered from the solvent. This is, however, somewhat uncertain, as the amount of material recovered from the solvent varied somewhat with the size of the sample, the percentage being less with the larger samples. It varied enormously with the thickness of the asbestos mat. The final columns show the percentage of bitumen corrected by deducting the amount of recovered material.

In the Soxhlet method samples varying from 2.7326 to 12.1604 grams were employed. The object was to study whether a large sample tended to give higher or lower results than a smaller one. No constant variation could be noticed but the duplicates do not agree as well as though we had used uniformly about 10 grams, as is generally recommended by the best known writers.

In Nos. 1, 6 and 7, Table III, it is possible that rather thin mats were used. If these were not included in the average, this method would show the smallest percentage of material recovered from the solvent instead of the greatest. It is also proper to state that the material worked with contained occasional small stones. These were difficult to pulverize and thoroughly incorporate into the mass. This explains in part the difficulty in securing exact duplicates in most of the work and especially when small samples were used. It seemed almost necessary in making the determinations shown in Table III to use small samples on account of the difficulty in filtering larger ones.

[1] "The Modern Asphalt Pavement," by Clifford Richardson. Published by Wiley & Sons. 1905. p. 504.

TABLE I.—MODIFIED SOXHLET USED BY AUTHORS.

No. sample.	Weight of sample.	Per cent. of material recovered from solvent.	Per cent. of bitumen (corrected).
1.....	4.4284	0.1943	10.18
2.....	4.4984	0.1154	10.17
2.....	11.1145	0.1154	9.87
3.....	4.5232	0.1769	9.22
3.....	12.1604	0.0810	9 62
4.....	4.5418	0.5636	9.48
4.....	9.0271	0.3900	9.53
5.....	2.7326	0.4020	10.08
6.....	4.3389	0.5700	10.68
6.....	10.4122	0.3055	10.31
7.....	4.4198	0.5747	9.59
7.....	10.4628	0.5008	9.50
8.....	4.2932	0.7147	9.13
8.....	11.4395	0.4601	9.22
9.....	4.2276	0.7002	9.78
9.....	11.3550	0.4437	9.87
10.....	4.7956	0.6339	9.53
		Mean, 0.4089	9.77

TABLE II —METHOD OF DOW.

No. sample.	Weight of sample.	Per cent. of material recovered from solvent.	Per cent. of bitumen (corrected).
1.....	9.9470	0.2312	10.17
1.....	8.4992	0.1400	10.06
2.....	9.8917	0.6340	9.95
2.....	9.4214	0.0573	10.02
3.....	10.1434	0.1770	9.24
3.....	10.0223	0.3800	9.44
4.....	10.0512	0.4537	9.95
4.....	7.4926	0.3096	....
5.....	9.9912	0.1363	9.55
5.....	9.1555	0.6641	9.43
6.....	9.9660	0.5558	10.46
6.....	9.9125	0.3955	10.49
7.....	9.9902	0.6456	9.35
7.....	10.5673	0.5337	9.57
8.....	10.0900	0.3211	9.04
8.....	9.5942	0.5784	....
9.....	9.9886	0.8109	9.64
9.....	10.0006	0.4420	9.73
10.....	10.1386	0.3056	9.58
10.....	7.3609	0.7322	9.52
		Mean, 0.4252	9.74

TABLE III.—FILTRATION AND WASHING ON AN ASBESTOS FILTER.

No. sample.	Weight of sample.	Per cent. of material recovered from solvent.	Per cent. of bitumen (corrected).
1.....	1.7764	1.2180	10.76
1.....	1.0184	1.2000	9.50
1.....	1.0878	1.2170	9.55
2.....	2.0084	0.3711	9.84
2.....	0.9977	0.0200	9.84
3.....	0.9768	0.3798	9.58
3.....	0.9960	.....	9.67
4.....	1.0274	0.3018	9.76
4.....	1.0148	0.0986	9.92
5.....	1.0626	0.2164	9.80
5.....	1.0038	0.4583	9.06
6.....	1.0559	1.1960	10.14
6.....	1.0066	1.4900	10.78
7.....	1.2520	2.2720	9.88
7.....	1.0057	0.2980	10.62
8.....	1.0034	0.6870	9.98
8.....	0.9966	0.2308	9.34
9.....	1.0260	0.3059	10.21
9.....	0.9945	0.2513	9.91
10.....	0.9876	0.3745	9.80
10.....	1.0120	0.1778	9.79
		Mean, 0.5926	9.80

A study of these figures shows the following:

(1) It is very difficult to obtain duplicate results, on account of the difficulty in getting a homogeneous sample of a synthetic mixture like asphalt. There is less variation when large samples are used.

(2) The mean percentage of soluble bitumen shown in the determinations by the method used in Table I was 9.77; by the method in Table II, 9.74; and by the method in Table III, 9.80. This is a remarkable agreement. With the samples used, long subsidence showed no advantage.

(3) As carried out by the authors the modified Soxhlet method shows the smallest percentage of material recovered from the solvent. This is, of course, desirable as it indicates the smallest loss on ignition of organic matter not bitumen, as well as carbon dioxide from carbonates and water from hydrated silicates. The variations, however, are slight and can be overcome by using thicker asbestos mats. This, however, makes the filtration difficult.

The method of Thomas and Dugan[1] was also tested. The only essential difference between their method and the Soxhlet method employed by us is that they use a continuous instead of a siphon extractor, and a soft quantitative filter-paper. We regard both of these variations as less satisfactory than the method employed by us.

The Soxhlet method as given by the authors can be completed within three to four hours from the time the sample is received in the laboratory. The greater part of the solvent can be recovered and used in other determinations. There is a slight tendency for the fine clay to creep upward between the folds of the paper capsule, and a possibility of a trace of clays being left in the siphon tube. In our samples the latter was not noticed except when the extraction was interrupted before completion.

As the method of washing out the bitumen by carbon bisulphide, drying the residue, and igniting the filter-paper apart from its contents, is occasionally used, we decided to conduct a few determinations to determine if an error is introduced by this procedure. The filter-paper was in each case washed with carbon bisulphide and weighed with the usual precautions. After very carefully washing out the bitumen, the filter-paper and its contents were dried and weighed, a correction was made for the mineral matter recovered from the bitumen, and the weight taken by difference. After this weight was obtained, the filter-paper was ignited apart from its contents, the ash from the paper added to the latter and the whole weighed. Starting, then, with a given weight of the sample we obtain two results: (1) the percentage of bitumen when the filter-paper is weighed; (2) the percentage of bitumen when the filter-paper is burned.

Sample No.	Paper weighed.	Paper ignited.
11	9.78	10.03
12	9.49	9.72
13	10.27	10.60

Thinking that the objection might be raised that possibly the filter-paper holds bitumen in its fibers which cannot be removed by washing, a direct experiment was made by extracting a filter with carbon bisulphide and weighing. This paper was then drenched with a solution of bitumen in carbon bisulphide which

[1] This Journal, 27, 293 (1905).

had been filtered through a Pasteur filter, and again extracted with pure carbon bisulphide.

Filter No. 1, C. S. and S., 9 cm., No. 597. Increase in weight, 0.0003 gram.

Filter No. 2, C. S. and S., 9 cm., No. 597. Increase in weight, 0.0000 gram.

The higher percentage of bitumen, therefore, shown when the paper is ignited represents a loss of ignited material, *i. e.*, organic matter, carbon dioxide from carbonates, water from hydrated silicates, and probably some bitumen so firmly held by surface tension in the fine clay that it is practically insoluble in carbon bisulphide.

In the following the sample was very finely pulverized during cold weather and mixed with the utmost thoroughness. It is believed that the difficulties of securing a homogeneous sample were thus largely avoided. The results from the sample are as follows:

	Bitumen. Per cent.
Modified Soxhlet	10.2
Dow's method	10.1
Richardson's centrifugal method[1]	10.1
Richardson's filter-paper method (paper weighed)	10.2
Richardson's filter-paper method[2] (paper ignited).	10.7

These figures seem to us to show that in no case should ignition be resorted to when the analyst is asked to determine the percentage of bitumen in paving material soluble in a given solvent. This, however, does not represent the exact amount of bitumen that was originally brought in contact with the clay as has recently been pointed out by Mr. Richardson in a private communication, for which acknowledgment is here made.

It should be added that Richardson's centrifugal method has given in our hands results practically identical with the results obtained by using the modified Soxhlet or the method of Dow, at a great saving in time.

The writers hope in the near future to repeat some of the work here given, using Trinidad asphalt.

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[1] "The Modern Asphalt Pavement," by Clifford Richardson, p. 541.

[2] Ibid. p. 539.

CHROME TANNING.

By Otto P. Amend.

Received February 17, 1906.

Knapp, in 1858, published a paper in which he clearly described a chrome-tanning process. The liquor which he used contained a basic chloride of chromium but he stated that the leather he thus produced did not differ materially from the well-known alum-tanned leather.

The first, so-called chrome leather put on the market was made according to the Heinzerling British patents of 1878.

According to this process, the skins were treated in solutions containing alum, common salt, and a chromate or bichromate of the alkalies or of the alkaline earth metals, and they were afterwards subjected to the action of a benzine solution of stearine or similar fats. No systematic attempt was made to reduce the chromic acid to a tanning form, the product being, at first at least, merely an alum tannage, colored and perhaps somewhat hardened with chromic acid, though on keeping for a length of time, reduction gradually took place at the expense of the hide fibre, and of the fats employed in currying, so that the leather internally became grayish green and really chrome-tanned.

Eitner took out a patent in 1881, in which he described a combination of the basic chromium and iron salts of the formula $Cr\langle^{OH}_{SO_4}$ or $Fe\langle^{OH}_{SO_4}$. The skins were immersed in a solution of these salts and afterwards treated, in a second bath, with a fatty emulsion, made from animal, vegetable and mineral oils.

The first really important advance in practical chrome-tanning was undoubtedly made by August Schulz in 1884. Schulz treated his skins in a bath containing potassium bichromate plus an acid, until they were saturated, and after this, they were placed in a second bath containing sulphurous acid or hyposulphite of soda plus an acid. This process has since been called the two-bath process It has since then been used successfully for many years, especially in the manufacture of goat or kid leather and has been greatly perfected. Yet it is rather an uncertain and unsatisfactory process as it does not produce the same leather at all times.

It is almost impossible to tan a heavy cow or steer hide by this process, as the chromic acid in the interior layers of the hide will bleed, or run out, while the hyposulphite is slowly acting upon the outer layers; this, as a matter of course, will produce a leather in which the inner layers remain untanned.

When hyposulphite of soda is used in the second bath of the Schulz process, free sulphur is precipitated in the

skin. Some authors claim that this free sulphur helps to make the leather soft and that this is the main cause for the difference in softness between two-bath and one-bath process leather. I do not agree with the authors referred to, but I think that Fahrion's theory is correct and that the difference in the results obtained by the one-bath process, as compared with those obtained by the two-bath process, is due to the oxidation of the hide fibres which occurs in the first bath of the Schulz process. I am also of the opinion that a similar oxidation occurs in vegetable tannages and is extremely beneficial. In regard to the free sulphur deposited between the hide fibres, it is my opinion that its effect is very harmful and that it is bound to form free sulphuric acid in the hide, by oxidation.

The one-bath process consists in treating the skins with a basic solution of a chromic salt. Such a salt can be produced by adding washing-soda to a chromium salt until sufficiently basic and then heating.

Procter says the solution must not be heated, but, unless heat is used, a complete chemical combination does not take place.

Differences in basicity have an important bearing on the tanning properties of chrome solutions. Chrome alum, on account of its acid character, penetrates the skin quickly, but fails to tan the skin thoroughly, is easily washed out, and produces a leather of a greenish color. When more basic solutions are used, the penetration is slower, the tannage more complete, the chrome less easily washed out and the leather produced is of a more bluish shade. When the solution becomes very basic, the chromium salt will precipitate on dilution (except if diluted in or with such saline solutions as described in my application for patent, but remains stable and perfectly dissolved in a concentrated solution.

Professor Procter has also recommended the use of a basic chromium salt solution, prepared by direct reduction of a bichromate with sugar, in the presence of such a limited quantity of hydrochloric acid as to produce a basic salt. In regard to the reduction of a chromic acid salt with organic matter, I am of the opinion that no one can succeed in making such reductions just alike; reduction with organic matter must be made in the presence of considerable acid and it is impossible therefore to produce a very basic salt by this method.

Glucose and glycerol have been recommended, also, as good reducing agents, but uniform and reliable liquors are best obtained by reducing with some salt of sulphurous acid or with sulphurous acid itself. It must be borne in mind also, that chromium salts of organic acids are worthless as tanning agents and that, as the organic acids which form during the reduction of

the chromic acid with organic substances combine with chromic oxide, this entails a very considerable waste of chrome.

I have examined and analyzed a number of chrome liquors which are now being placed upon the market and I find that nearly all of them are produced by the reduction of potassium or sodium bichromate by means of glycerol, alcohol or glucose, most of them being sulphates. Some are of the formula $Cr_2(SO_4)_3$ + organic acids, while others are of a more basic formula as $Cr_2(SO_4)_2$ + organic acids. Some contain free glucose and others traces of formaldehyde.

The basic chrome salt produced by adding carbonate of sodium to chrome alum or chromium sulphate, while heating, proved to be a very good tanning material. It quickly deposits a very basic chromium sulphate in the skin and leaves a decidedly acid salt in the solution and the color of the skin is pale lilac, almost white.

If a basic sulphate of chromium is used, of the same formula as the above, but prepared by reducing a bichromate or chromic acid by means of sulphurous acid, the skin takes up the basic sulphate as such, and the tanning bath will not show an increase of acid; the color of the skin in this case is a pale bluish green.

205 THIRD AVE., NEW YORK.

NEW BOOKS.

HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS WITH SPECIAL REFERENCE TO PRACTICAL WORK. By J. W. MELLOR, D.Sc. Second edition, enlarged. London and New York: Longmans, Green & Co. 1905. 8vo., xxii+632 pp. Price, $4.50.

Since the first edition of this work, which appeared in 1902, has been critically reviewed in this Journal (**25,** 103 (1903)), it is only necessary to call attention to the appearance of a new edition and to the changes that have been made in it. These are fairly extensive ones, but they consist in the revision and expansion of the subjects previously treated and in minor modifications in the order of presentation rather than in the inclusion of new branches of mathematics, or in any radical change in the point of view. Without depreciating the value of the book to advanced students of chemistry and physics, the reviewer wishes to express the opinion that there is no direction in which it could be made of so great service to education as by placing it in the hands of all those teachers of the higher mathematics who lay more stress on the relatively insignificant matter of mathematical technique—such as the more complicated processes of algebraic reduction,

differentiation, and integration—than on applications of mathematical conceptions, by which alone their real significance can be made intelligible. A. A. NOYES.

CONVERSATIONS ON CHEMISTRY: PART II. THE CHEMISTRY OF THE MOST IMPORTANT ELEMENTS AND COMPOUNDS. By WILHELM OSTWALD. Translated by STUART TURNBULL. New York: John Wiley & Sons. 1906. viii+373 pp. Price, $2.00.

The second part of Professor Ostwald's latest book is largely descriptive and deals with the more familiar elements and compounds. There is included, however, a very lucid series of dialogues on combining proportions and the laws connected therewith. The atomic, molecular, and ionic hypotheses are also set forth, and are used to explain chemical facts. Electrolysis is discussed and much attention is given to acids, bases, and salts.

The characteristics which made Part I so brilliant a piece of work, and which were described in the former review,[1] are equally conspicuous in the part before us. The author is to be congratulated on having given to all his readers, and particularly to teachers, an example of how to bring elementary chemistry up to date without destroying its simplicity.

The translator seems to be unfamiliar with Ostwald's other works, and on the last page confuses the "Outlines of General Chemistry," translated by Walker, with the "Principles of Inorganic Chemistry," translated by Findlay, the latter being the work whose title is given in the original. In all other respects the translator has performed a difficult task with distinct success. A. S.

CHEMISTRY OF THE ALBUMENS. By S. B. SCHRYVER, Lecturer in Physiological Chemistry to University College, London. Philadelphia, Pa.: P. Blakiston's Son & Co. 1906. Price, $2.00.

This book, as its name indicates, deals almost wholly with the chemistry of the "Albumens," that is, with the decomposition products which they yield and with the structure of these products.

Facts relating to the solubility, physical properties, precipitation by salts, coagulation, behavior towards acids and bases, etc., which have, in the past, formed so large a part of the accounts that have been written of these bodies occupy in this book but a very insignificant place. This fact shows the great progress made

[1] This Journal, 27, 1020 (1905).

during the past five years in our knowledge of the chemical side of this subject, for it is now possible to give a condensed account of the purely chemical facts that are known which is sufficiently extensive to warrant their publication in a separate volume.

Schryver's book contains a series of lectures delivered in the Physiological Department of University College, London. The first lecture, which deals with the general properties of the "Albumens" occupies only 16 pages. The seven lectures which fill the succeeding 123 pages deal with purely chemical facts, while the last two lectures, which discuss "General Theories of Biochemical Action," form the remaining 28 pages.

The author uses the word "Albumen" as a generic term to designate the class of bodies commonly called proteids by English and American writers, thereby hoping to bring English and German usage into harmony, for the Germans use the word "Proteide" as a name for a particular group of these bodies. With this purpose the reviewer is in accord and, led by the same reasons, has employed the word protein as a designation for these substances. This latter word seems to him, however, to bring English and German usage into closer harmony than the word albumen, a translation of *Eiweiss*, for the Germans are already using the word protein as a substitute for their *Eiweisskörper*, and this practice seems to be increasing. Fischer used this term throughout his late address before the German Chemical Society.

Schryver writes throughout his book as though convinced that the protein molecule contains, in most cases if not in all, a carbohydrate complex and, like most writers, considers the Molisch reaction to give satisfactory evidence of this. This, a furfurol reaction, is given by almost all proteins, but Schryver seems to have overlooked the fact that furfurol, as such, cannot be obtained from any of the proteins, except those from which a carbohydrate has already been isolated. Proteins of the latter kind are few and there is good reason to consider them to be combinations of a protein molecule proper, with a non-protein group, which latter contains the carbohydrate complex.

Schryver also treats the proteins as pseudo bases and acids, citing Cohnheim as authority, but this view has been abandoned by Cohnheim, for in the last edition of his "Chemie der Eiweisskörper" he says that the fact that the amino acids behave in exactly the same way has made this hypothesis unnecessary.

A considerable part of Schryver's book is occupied with the chemistry of the nucleic acids and their decomposition products, especially the purine and pyrimidine bodies. In this he has followed a general practice of writers on proteins for which, however, there is little warrant, as these bodies bear no chemical relation to the protein molecule proper. The only reason for including the nucleic acids is the fact that they are always found in nature together with the proteins or the protamines. This practice, while convenient for those familiar with the proteins, leads to confusion among those who take only a general interest and read such books as the one under consideration in order to obtain a general knowledge of the chemistry of the proteins. Schryver's book gives a good review of the present knowledge of this branch of chemistry, contains few errors and omits but few of the important facts that are known.

THOMAS B. OSBORNE.

A TEXT-BOOK OF CHEMISTRY FOR THE USE OF STUDENTS AND PRACTITIONERS OF MEDICINE, DENTISTRY AND PHARMACY. By WILLIAM RUSSELL JONES. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1905. 462 pages. Price, $2.50.

This is one of the books usually classed as "Medical Chemistry" and contains, according to the preface, "all that is needed in chemistry for students of medicine, dentistry and pharmacy." It is divided into six parts, including sections on Physics, Chemical Philosophy, Inorganic Chemistry, Organic Chemistry, Methods of Quantitative Analysis and Physiological Chemistry. The tests of qualitative analysis are included under Inorganic Chemistry; the section on Quantitative Methods consists of but 7 pages, not very clearly written. While the book contains a fairly satisfactory compilation of facts, it abounds in loose and inaccurate statements and can be recommended only to those teachers who believe that medical students require but little knowledge of chemistry.

J. H. LONG.

THE CYANIDE INDUSTRY. By R. ROBINE AND M. LENGLEN. Translated by J. ARTHUR LECLERC, with an appendix by C. E. MUNROE. New York: John Wiley & Sons. 1906. 8vo. xi+401 pp. Price, $4.00.

The great development in the manufacture of commercial cyanides, during the last fifteen years, has followed as a natural result of their increased use in gold extraction by the MacArthur-Forrest process. Considerable literature upon cyanides is

scattered through numerous scientific and trade papers, but to find the various articles costs much time and trouble. In this volume the authors have undertaken to bring this material together for the busy reader. The work is divided into four parts: The Chemistry of Cyanogen; Present Condition of the Cyanide Industry; Methods of Manufacturing Cyanide Compounds; The Use of Cyanogen Compounds; a short chapter of Conclusions, and an Appendix, containing a valuable Digest of U. S. patents relating to the cyanide processes for the recovery of precious metals. This Digest by Professor C. E. Munroe adds much to the usefulness of the book. It seems unfortunate that Part II, upon the Present Condition of the Cyanide Industry, should be so condensed—only about four pages of descriptive matter, chiefly dealing with conditions in France, and seven pages devoted to lists of manufacturers and statistics of imports into France. The discussion of the methods of manufacture of cyanides, and of the numerous processes proposed or patented, is satisfactory, just the essentials of each process being reviewed concisely, with frequent comment upon the difficulties to be met. A compilation of this kind, of a large number of investigations, patents and working processes, relating to a single industry, is most useful to technologists, lawyers, and manufacturers, but is probably too technical for the general reader. The translator has done his work in a very acceptable way, but the influence of the foreign idiom is occasionally noticeable; thus on pages 274 and 281 appear references to "heating by means of coils of steam." A few misprints, inevitable in a first edition, will be noted: there is a discrepancy in the dates assigned to the discovery of Prussian blue on pages 69 and 81, while on page 2 of the introduction this discovery is attributed to Scheele, where potassium ferrocyanide was intended. With proper names there is also some difficulty at times, *e. g.*, we find Fowlis and Forest, several times each. Other slips in typography occur on pages 194, 289, 306, 308, 351, while on a great many pages failure of a type to print will be noticed. Aside from these minor faults the typographic work is very good. To those who may, hereafter, have occasion to look up points connected with the cyanide industry, the book will be of great assistance, and to those who may be already familiar with the industry, there is much that will be of interest in its pages. F. H. T.

RECENT PUBLICATIONS.

La Grande Industrie Chimique. By d'Hubert et Pécheux. Paris: J. B. Baillière et fils. 384 pp. 6 fr.

Les Acides Chlorhydrique, Azotique, Sulfurique et les Chlorures Décolorantes. By Pécheux. Paris: J. B. Baillière et fils. 96 pp. 1 fr. 50.

Guide Pratique de l'Expert-Chimiste en Denrées Alimentaires. By G. Pellerin. Paris: J. B. Baillière et fils. 680 pp. 12 fr.

Qualitative Analyse unorganischer Substanzen. By Heinrich Biltz. Second edition. Leipzig: Veit & Co. 1906. 3+64 pp. Marks 2.20.

Tabelle zur Berechnungen der volumetrischen Stickstoff. By L. Gattermann. Leipzig: Veit & Co. 1906. Marks 1.20.

Lehrbuch der organischen Chemie. By Vict. Meyer und Paul Jacobson. Second edition. Leipzig: Veit & Co. 1906. Marks 10.80.

Leçons de Chimie, 1re Année. By Tanquerey et P. Poiré. Paris: Ch. Delegrave. 2 fr. 50.

Chemistry Lecture Notes. By G. E. Welch. London: Blackie. 1906. 64 pp. 1/6.

Elémentes de Chimie Générale: 1re fasc. Metalloides. By C. Noble. Paris: Vuibert et Nony. 288 pp. 2 fr. 50.

Chemistry of the Albumens. Ten Lectures. By S. B. Schryver. London: J. Murray. 1906. 200 pp. 7/5.

Einleitung in die chemische Analyse. By Ludwig Medicus. 3. Hft. Kurze Anleitung zur Gewichtsanalyse. Edition 5. Tübingen. H. Laupp. 1906. 8+185 pp. Marks 3.60.

Ätherischen Öle nach ihren chemischen Bestandteilen unter Berücksicht der geschichtlichen Entwicklung. By F. W. Semmler. Bd. 1. Allgemeiner Teil. Methanderivate. Leipzig: Veit & Co. 1906. 16+860 pp. Subskr. Pr. M. 34.50. Einzelpr. M. 40.

Lehrbuch der anorganischen Chemie. By A. Stavenhagen. Stuttgart: F. Enke. 1906. 10+525 pp. Marks 11.60.

Handbuch der Drogisten-Praxis. Ein Lehr- und Nachschlagebuch für Drogisten, Farbwarenhändler usw. By G. A. Buchheister. Mit einem Abriss der allgemeinen Chemie v. Dr. Rob. Bahrmann. Berlin: J. Springer. 1906. 12+943 pp. Marks 10.